SYNTHESES

of

POLYCYCLIC AROMATIC HYDROCARBONS.

THESIS

presented by

William Kelly, B.Sc., (Glasgow)

for the Degree of

DOCTOR of PHILOSOPHY

of the

UNIVERSITY of GLASGOW.

January, 1958.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

It is with a deep feeling of gratitude that I record my appreciation of the unfailing encouragement given to me by Dr. E. Clar during the course of this work. He has freely and generously given me the benefit of his intimate knowledge and wide experience of this field of chemistry.

I should also like to thank Professor Robertson and Dr. Rossmann for their invaluable help in determining the structure of circumanthracene.

Finally, I thank the University of Glasgow for the award of a maintenance grant during the final year of this work.

C O N T E N T S.

PUBLICATIONS.

The material presented in this thesis has been published in the following papers. Reprints are enclosed at the end.

1. Diperinaphthyleneanthracenes. E. Clar, W. Kelly and (in part) J.W. Wright. J.Chem.Soc., 1954,1108.
2. Circumanthracene and Dinaphtho(7':1'-1:13)(1":7"-6:8)peropyrene. E. Clar, W. Kelly, J.Monteath Robertson and M.G. Rossmann. J.Chem.Soc., 1956,3878.
3. 3:4-5:6-10:11-12:13-Tetrabenzoperopyrene. E.Clar and W. Kelly. J.Chem.Soc., 1956,3875.
4. Benzo a perylene and some of its Derivatives. E. Clar, W. Kelly, D.G. Stewart and (in part) J.W. Wright. J.Chem.Soc., 1956,2652.
5. Die Synthesen des Terrylens und Quaterrylens und über das vermeintliche Quaterrylen von A. Zinke. E. Clar, W. Kelly and R.M. Laird. Monatshefte für Chemie, 1956,87,391.
6. Heptaphene and 2:3-8:9-Dibenzopicene. E. Clar and W. Kelly. J.Amer.Chem.Soc., 1954,76,3502.
7. 2:3-Benzopicene and Naphtho(2':3'-1:2)chrysene. E. Clar and W. Kelly. J.Chem.Soc., 1957,4163.

SUMMARY.

1:9-5:10-Diperinaphthyleneanthracene was synthesised by ring closure of 1:5-dichloro-9:10-di-1'-naphthylanthracene with potassium hydroxide in quinoline. The hydrocarbon was compared with the previously known 1:9-4:10 isomer, which was also resynthesised by the above method. The spectrum of the 1:9-5:10 isomer did not agree with the theoretical predictions of Dewar (J. Chem. Soc., 1952, 3539). 1:9-5:10-Diperinaphthyleneanthracene forms an endocyclic mono addition product with maleic anhydride, but on prolonged heating with maleic anhydride and chloranil two molecules of the anhydride are irreversibly condensed with the hydrocarbon and the dianhydride of dinaphtho (7':1'-1:13)(1":7"-6:8)peropyrene tetracarboxylic acid is formed. Decarboxylation of this acid with copper powder and quinoline gave the dinaphthoperopyrene, but if soda lime was used a second hydrocarbon was also obtained. This was shown by X-ray crystallographic studies to be circumanthracene, the third member of the series formed by coronene and ovalene. In the course of an attempted alternative synthesis of circumanthracene, the hydrocarbon 3:4-5:6-10:11-12:13-tetrabenzoperopyrene was prepared.

The structural and spectral relationship of several

dioxides of increasing degree of condensation, derived from 1:5-di-2'-naphthyloxyanthraquinone was studied, and a hydrocarbon obtained by reduction and dehydrogenation of one of them was shown by an independent synthesis to be 1:2-benzoperylene.

Terrylene was synthesised by an unambiguous route and shown to be similar to the hydrocarbon alleged to be quaterrylene by Zinke et al. (Monatsh. 1955,86,853) but different from the terrylene previously prepared by Clar (Chem. Ber., 1948,81,52). A hydrocarbon which is considered to be quaterrylene was synthesised by condensation of perylene.

The condensation of phenanthrene and chrysene with phthalic anhydride and with o-toluoyl chloride under the influence of aluminium chloride at high temperatures and using tetrachloroethane as solvent was studied. This resulted in the synthesis of heptaphene and 2:3-8:9-dibenzopicene from phenanthrene and 2:3-benzopicene from chrysene.

Throughout these investigations, spectra were recorded and in many cases were invaluable in assigning correct structures.

The Anellation Principle of E. Clar.

The anellation principle of E. Clar is an invaluable tool in the study of the structures of polycyclic aromatic hydrocarbons. The band maxima and main features of the absorption spectrum of a hydrocarbon can often be predicted from a knowledge of the spectra of related hydrocarbons and conversely the absorption spectrum of a hydrocarbon, the structure of which is unknown or in doubt, may be used to suggest a possible structure, or, when several structure are possible by the method of synthesis, to decide between them.

In the present work, the application of the anellation principle to the hydrocarbon obtained from the decarboxylation of dinaphthoperopyrene tetracarboxylic acid with soda-lime suggested it probably was circumanthracene, which proved to be the case. Again the principle was used to assign structures to the isomeric hydrocarbons obtained from the Friedel-Crafts condensation products of phenanthrene and chrysene. Ideally the principle should be used to supplement and not supplant normal chemical methods of structural proof, though in the present work, this was not always possible.

From a study of the behaviour of the absorption bands of aromatic hydrocarbons under various physical conditions, E. Clar (1-5) grouped them into three classes, which he termed α, β and para (p)-bands. They have the following characteristics.

(a) The p-bands, which shift to the red with a decrease in temperature, are the long wave bands in the spectra of anthracene and the higher acenes and the second group of bands in benzene and naphthalene. The p-bands shift strongly to the red on linear anellation in the acene series and slightly to the violet on angular anellation in the phene series (positive and negative anellation effect (4)). A considerable increase or decrease in reactivity, e.g. photo-oxidation and addition of maleic anhydride, is associated with these shifts and the p-bands are therefore attributed to an electronic transition from the ground state to an excited p- or Dewar form. In the acenes, the intensities of the p-bands lie between log ε = 3.5-4.3.

(b) The α-bands, which are less intense, shift slightly to the violet with decreasing temperatures. A strong shift to the red, which is accompanied by an increase in the reactivity of the central nucleus is obtained on

anellation in the phene series. In the acene series, a similar shift is obtained on linear or angular anellation. The bands are the first group in the absorption spectra of benzene, naphthalene and the phenes. For anthracene and the higher acenes, they are hidden or partly hidden, by the more intense p-bands. The intensities of the α-bands lie between log ε = 2-3.

(c) The β-bands, which are the most intense group of bands and which lie more in the ultra-violet, shift considerably to the red with decreasing temperatures. They show the same anellation effect as the α-bands and it has been found that for uniplanar aromatic hydrocarbons, the ratio of the frequencies of the α- and β-bands is constant, viz. $\nu_\alpha : \nu_\beta = 1:1.35$. The intensities of the β-bands lie in the region logε = 5.

The wavelengths of the absorption bands can be calculated from the simple relationship $\lambda = K^2/R$, where K, which is called the Order Number of the hydrocarbon, is a simple function of the number of π electrons in it and R is a constant which can be related to Rydberg's Constant.

The wavelength of the first p-band in the acene series is calculated from $\lambda = K_p^2/R_p$, where R_p = 1,712,800 cm.$^{-1}$ The Order Number (K_p) is equal to 6, 7, 8, 9, 10 and 11 for benzene naphthalene, anthracene, tetracene, pentacene and hexacene respectively.

In the phene series, benzene, naphthalene, phenanthrene, tetraphene, pentaphene, hexaphene and heptaphene, the order number, K, is equal to $7\frac{1}{2}$, 8, $8\frac{1}{2}$, 9, $9\frac{1}{2}$, 10 and $10\frac{1}{2}$ respectively and $R_\alpha = 2194600$ cm.$^{-1}$ Although these compounds form one series, i.e. the differences in $\sqrt{\lambda}$ between two successive members are constant, the α bands belong to two types, each alternate member of the series having α-bands of the same type. These form the "whole-numbered" series: naphthalene, tetraphene, hexaphene, and the "half-numbered" series: benzene, phenanthrene, pentaphene and the hydrocarbon described in the present work, heptaphene.

The first β-band of the phenes and acenes is calculated from $\lambda_\beta = K^2/R_\beta$. K has the same values for the phenes listed above, but differs from the order numbers (K_p) used in the calculation of the first p-band of the acenes. It is equal to $8\frac{1}{2}$, 9, $9\frac{1}{2}$, 10 for anthracene, tetracene pentacene and hexacene. The constant R_β for this series is equal to 2962700 cm.$^{-1}$ The constants R_α and R_β are in the ratio 1:1.35.

The relationship between the order numbers of a hydrocarbon for the p-bands and the α and β bands is given by

$$K_p = 2\,K_\alpha - 9.$$

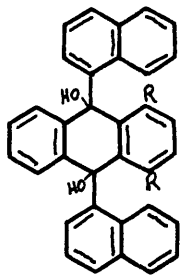
The Principle and its theoretical implications have been developed and extended by E. Clar and other anellation series have been found, e.g.

1) the p-bands of the perylenes

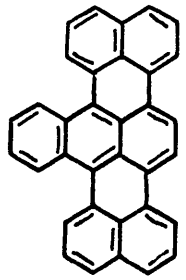
2) the p-bands of the pyrenes

3) the p-bands of the peropyrenes

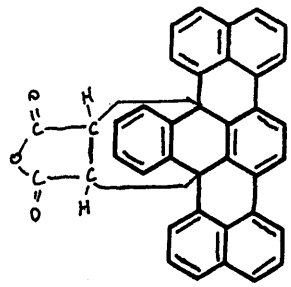
The present work has contributed a new series, the polyrylenes, to the Anellation Principle.



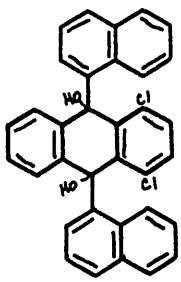
I



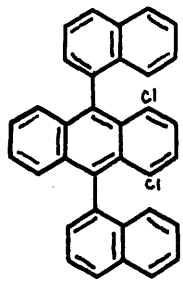
II



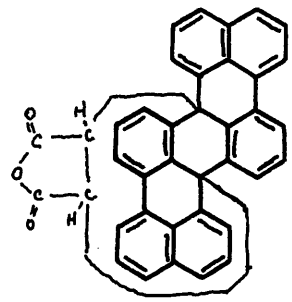
III



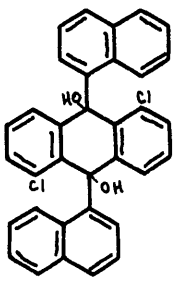
IV



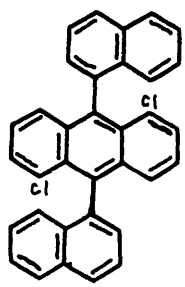
V



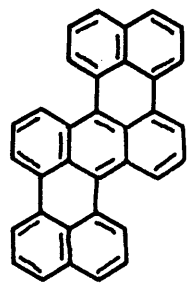
VI



VII



VIII



IX

The Syntheses of Diperinaphthyleneanthracenes.

In 1932 Clar and Guzzi (6) synthesised a diperinaphthyleneanthracene by the condensation, with aluminium chloride of 9:10-di-1'-naphthyl-9:10-dihydroanthracene-9:10-diol (I; R = H). Of the two possible products of the reaction, the 1:9-4:10 (II) and the 1:9-5:10-diperinaphthyleneanthracene (IX), they considered that they had obtained the latter, since the 1-4-dimethyl derivative of (I), (R = Me) did not give the corresponding dimethyl-diperinaphthyleneanthracene. In 1949, the structure was re-examined by Clar and Wright (7, 8) who showed that the hydrocarbon was really the 1:9-4:10 isomer (II), since the dehydrochlorination of 1:4-dichloro-9:10-di-1'-naphthyl-9:10-dihydroanthracene-9:10-diol (IV) gave a chlorine-free hydrocarbon, identical with that obtained by Clar and Guzzi. The yield was also improved by using a melt of sodium chloride and aluminium chloride (cf. (9)) for the condensation, instead of aluminium chloride with a trace of pyridine as was previously used.

The present work, the synthesis of the 1:9-5:10-isomer (IX), was prompted by the work of Dewar (10) who predicted, by a molecular orbital method, the first long wave band of the absorption spectrum of the two isomers and on the basis of his results assigned the correct structure

to the hydrocarbon synthesised by Clar and Guzzi. The validity of his results could only be judged, though, by actual comparison of the two isomers.

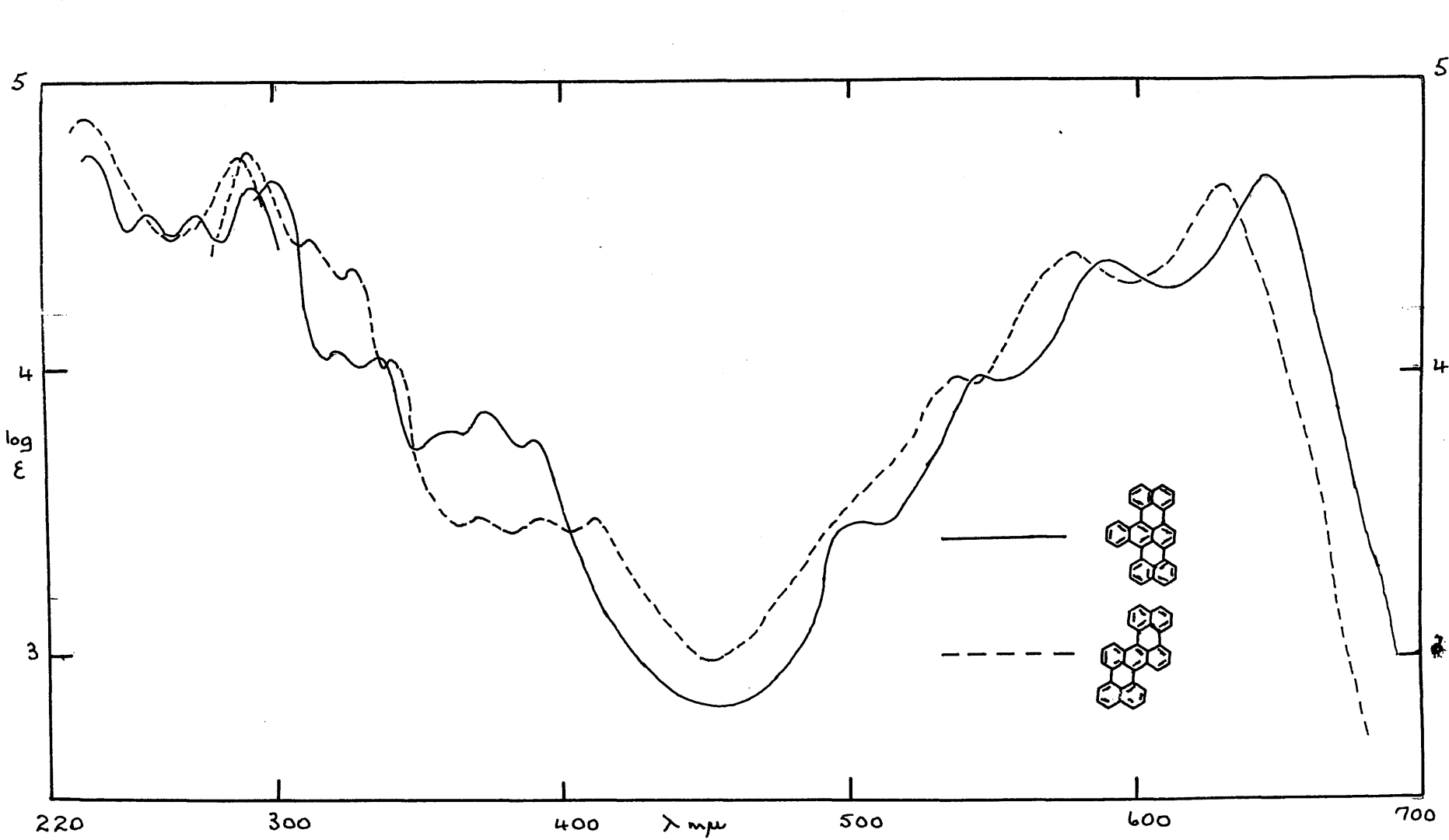
A synthesis, analogous to that of the 1:9-4:10 compound (II) by Clar and Wright (7, 8), by the condensation of 1:5-dichloro-9:10-di-1'-naphthylanthracene in an aluminium chloride-sodium chloride melt was unsuccessful, as it gave only chlorine containing compounds. It appears that the structure of the 1:9-4:10 isomer (II) rather than that of the 1:9-5:10 compound (IX) is energetically favoured during the second ring closure. This was overcome by the use of a more specific dehydrochlorinating agent.

1:5-Dichloroanthraquinone was condensed with 1-naphthylmagnesium bromide to give the diol (VII) (cf. Guyot and Staehling (11)), which was reduced to the corresponding anthracene (VIII) by boiling with hydriodic acid and acetic acid. The dichloroanthracene cyclised smoothly to the blue hydrocarbon, 1:9-5:10-diperinaphthylene-anthracene (IX) when heated with potassium hydroxide in boiling quinoline for 45 minutes (cf. Zinke et al. (12)). Ring closure to the 2' rather than the 8' position of the

naphthyl group, giving the dibenzorubicene is a possibility, but is excluded since this hydrocarbon has already been prepared by Scholl and Meyer (13) and is completely different from (IX). As will be seen later (p.17), when the 2' positions of the naphthyl groups of (VIII) are occupied by methyl groups, ring closure still gives a hydrocarbon which is very similar to (IX).

An X-ray analysis of the crystal structure of the blue hydrocarbon (IX) has been carried out by Robertson and Rossmann (personal communication) and agrees completely with the structure of (IX). Further proof of the structure is afforded by the spectrum of the maleic anhydride addition product (VI) (Fig. 2). If, as expected, the maleic anhydride forms an endocyclic addition product by adding to the meso positions of the central anthracene nucleus of (IX), then the molecule will be effectively divided into two similar non-interresonating parts, each of which can be considered as a substituted benzanthrene nucleus. Comparison of the spectrum of (VI) with that of benzanthrene (14) (Fig. 2) shows that this is almost certainly so. The difference in intensity of the two spectra ($\sim$ 0.3 log units, is that to be expected from the structure of the adduct (VI).

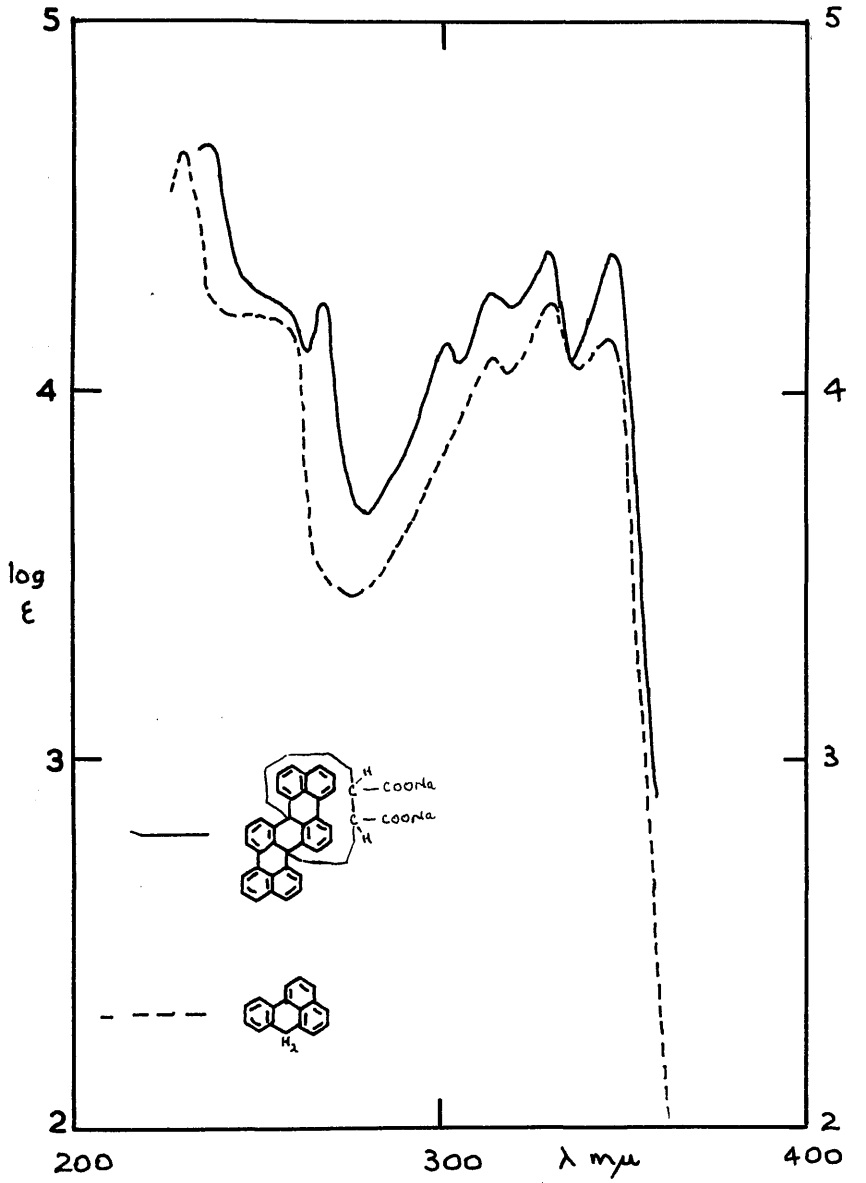
The spectra of the hydrocarbons (II) and (IX) are given in Fig. 1. The two spectra are rather similar,



1:9-4:10-Diperinaphthyleneanthracene (II). Maxima in mμ. 643.5, 589, 544, 503; 392, 374; 336, 322, 298 in benzene; 293, 272, 254, 236 in alcohol.

1:9-5:10-Diperinaphthyleneanthracene (IX). Maxima in mμ. 650, 579, 536; 412, 392, 372; 342, 328, 312, 292 in benzene; 288, 236 in alcohol.

Fig. 1



Disodium salt from the maleic anhydride adduct (VI) in alcohol. Maxima in mμ. 346.5, 329, 314, 302; ·268; 238.

Benzanthrene in alcohol. Maxima in mμ. 344, 329, 312; 250; 228.

Fig. 2.

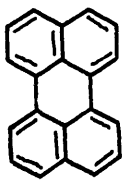
especially in the long wave band region. Dewar (10) calculated that the first absorption bands of (IX) and (II) as 843 and 641 mμ respectively. The observed values are 630 and 643 mμ respectively. The near infra-red was examined as far as 1000 mμ but no other absorption bands could be detected. It would be difficult then, if not impossible, to decide between the structures of (II) and (IX) from a purely theoretical consideration of their spectra.

When 1:9-4:10-diperinaphthyleneanthracene was synthesised by ring closure of the 1:4-dichloro compound (IV) with aluminium chloride, a small quantity of anthracene was also obtained (Wright, (7)). Since chlorine can be removed from (IV) during the reaction, other than by ring closure, the fact that a chlorine free hydrocarbon was obtained does not by itself provide a rigorous proof of the structure of (II). Therefore it was decided to synthesise (II) in an analogous manner to its isomer (IX).

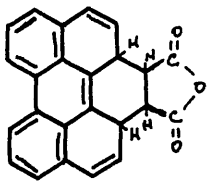
The diol (IV), previously prepared by Wright, was reduced to the 1:4-dichloroanthracene (V) and cyclised to the hydrocarbon (II) with potassium hydroxide and quinoline. It was identical with the hydrocarbon obtained by Clar and Wright and also by Clar and Guzzi. The time taken to effect the ring closure to the hydrocarbon (II) was about a

quarter of that required to form (IX) and this again demonstrates, as mentioned above, that the structure of (II) is more readily formed than that of (IX).

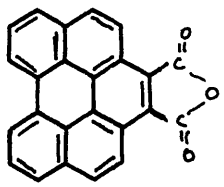
The hydrocarbon (II) also forms an addition product (III) with maleic anhydride, the spectrum of which is completely different from that of the adduct (VI). In this case the molecule is divided into dissimilar parts, a benzene derivative and a substituted 2:3-2":3"-dibenzterphenyl.



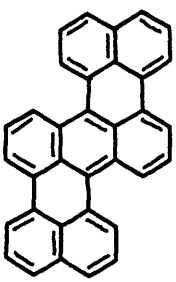
X



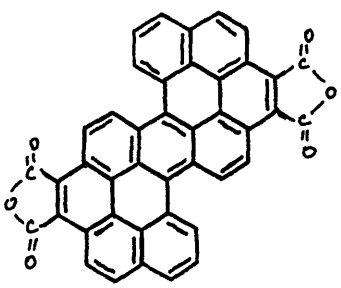
XI



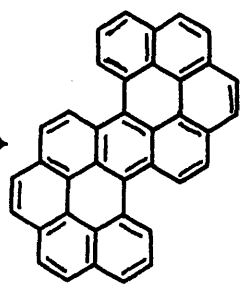
XII



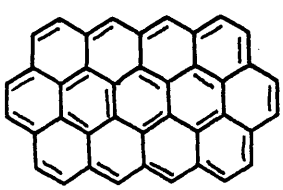
IX



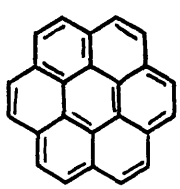
XIII



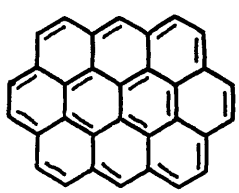
XIV



XV



XVI



XVII

Synthesis of Circumanthracene and Dinaphtho(7':1'-1:13)(1":7"-6:8)peropyrene.

Perylene (X) can react with one molecule of maleic anhydride in the presence of an oxidising agent to form 1:12-benzoperylene dicarboxylic acid anhydride (Clar,(15)). An unstable adduct (XI) is probably formed by a Diels-Alder reaction. This adduct, unless it is dehydrogenated to (XII), quickly dissociates again into its components. The fact that a high yield of a dibromo-1:12-benzoperylene is obtained when 1:12-benzoperylene is refluxed with bromomaleic anhydride suggests that this is probably correct (Clar and Zander, (16)).

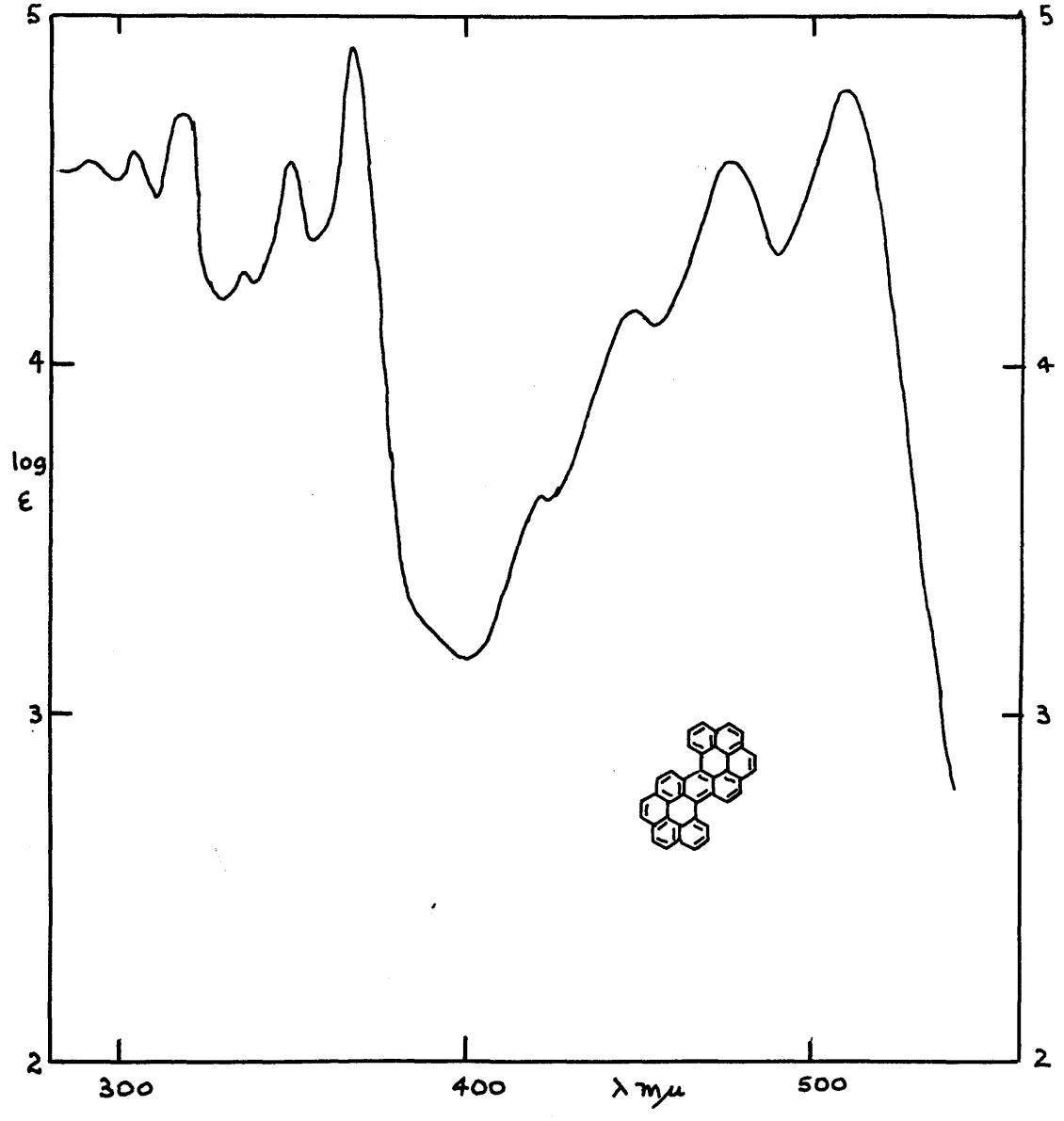
1:9-5:10-Diperinaphthyleneanthracene (IX) contains two diene systems similar to that between the 1:12 positions of perylene. Therefore it was decided to see whether (IX) would react with maleic anhydride in a similar manner. As stated in the preceding chapter, diperinaphthyleneanthracene (IX) when refluxed in a solution of maleic anhydride in xylene or heated with the anhydride alone, forms an endocyclic addition product by adding to the central anthracene nucleus. This adduct dissociates into its components when heated above 200°. When the hydrocarbon is boiled with maleic anhydride (b.p. 196°), the mono colourless adduct is first formed and is deposited from the

solution. If chloranil is then added and boiling continued, the adduct is gradually redissolved and a dark purplish compound, the tetracarboxylic acid dianhydride (XIII) is precipitated.

The dianhydride (XIII) was decarboxylated by boiling in quinoline with copper powder, to give the orange-red dinaphthoperopyrene (XIV). The spectrum of this hydrocarbon is given in Fig. 3. When compared with the spectrum of the starting material (IX) (Fig. 1), the strong shift to the violet of the long wave bands, caused by the two additional benzene rings, is immediately obvious. The shift (120 mμ), is rather more than twice the shift caused by the passage of perylene to 1:12-benzoperylene (52 mμ).

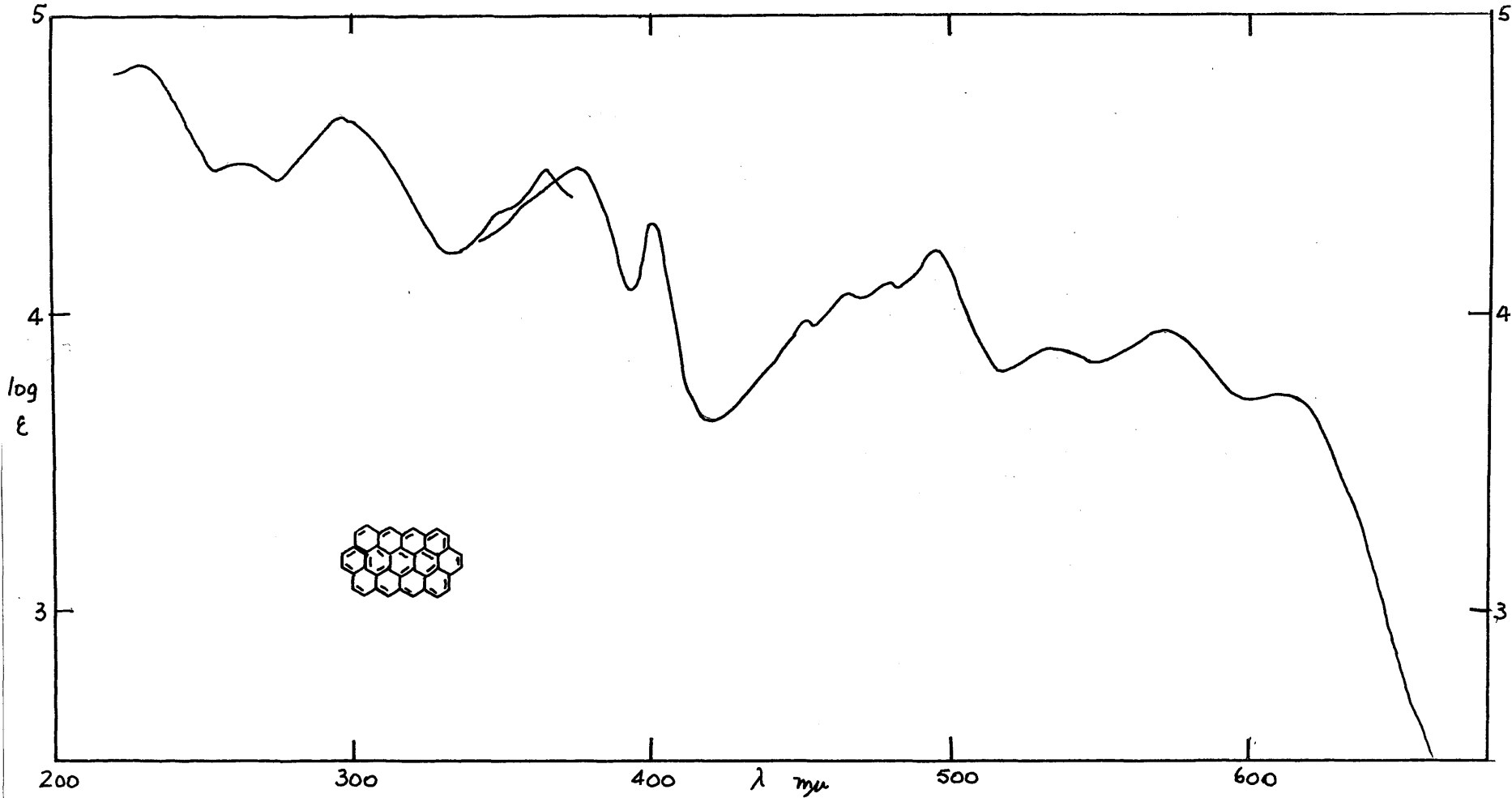
The dianhydride could also be de-carboxylated by sublimation from soda-lime at 400° in vacuum. In this case, however, besides the dinaphthoperopyrene, a second hydrocarbon was obtained. It was higher melting, less volatile, and less soluble than the dinaphthoperopyrene. The two hydrocarbons were separated by differences in solubility and by chromatography on alumina.

Certain features of the spectrum of this hydrocarbon (Fig. 4), especially the relationship of the β band with the β band of coronene and ovalene, indicated that a "controlled graphitisation" might have taken place and it



Dinaphtho(7':1'-1:13)(1":7"-6:8)peropyrene (XIV) in benzene. Maxima in mμ. 510, 476, 447, 410; 367, 349, 334; 317, 304, 290.

Fig. 3.



Circumanthracene (XV). Maxima in mμ. 607, 569, 535; 494, 478, 435, 451; 400.5; 374 in 1-methylnaphthalene; 365, 297, 263, 232 in dioxan.

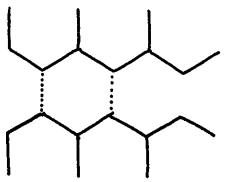
Fig. 4

might have the structure (XV). The most straightforward method of proving the presence of the two additional carbon atoms was by X-ray analysis of the crystals. Professor Robertson and Mr. Rossmann, of this Department, very kindly agreed to carry out this investigation and their results, which are given in an appendix to the thesis, revealed the presence of carbon atoms in positions 8 and 16. They also showed the molecular weight to be 492 ± 5. (Calc. for $C_{40}H_{16}$ (XV): M, 496.5. Calc. for $C_{38}H_{18}$ (XIV): M, 474.5). Since the molecule has a central anthracene nucleus completely surrounded by condensed benzene rings, the name "circumanthracene" has been given to the compound and the prefix "circum" used in this sense is suggested for similar compounds. Thus coronene (XVI) and ovalene (XVII) would be named circumbenzene and circumnaphthalene respectively. The new hydrocarbon is the third member of the series, beginning with coronene and ovalene.

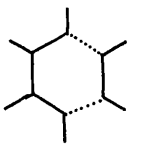
The origin of the carbon atoms in positions 8 and 16 is still doubtful. They may come from the carbonyl groups of the anhydride or from the complete breakdown of another molecule during the treatment with soda-lime at 400°.

During graphitisation and building up a condensed ring system, the formation of carbon rings can take place by three methods - the addition of (3 + 3), (4 + 2), and (5 + 1)

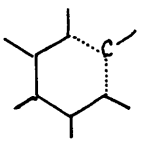
carbon atoms. This is illustrated in (XVIII), (XIX) and (XX) respectively. Examples of the first two mechanisms



XVIII

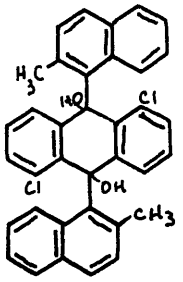


XIX

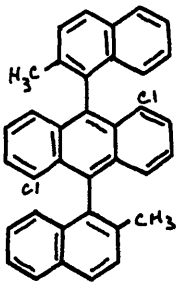


XX

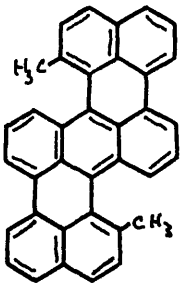
are known in synthetic chemistry. The frontal condensation of 3 + 3 carbon atoms takes place under the influence of heat or aluminium chloride. The second, (4 + 2) carbon atoms, constitutes a diene synthesis analogous to the reactions (X) $\longrightarrow$ (XII) and (XIII) $\longrightarrow$ (XIV). It may also involve an aromatic double bond at high temperatures. The third possibility, (5 + 1) carbon atoms, which does not seem to have been described before, probably involves free radicals and bivalent carbon compounds.



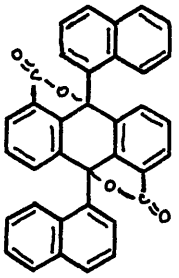
XXI



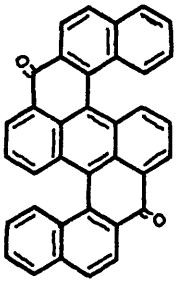
XXII



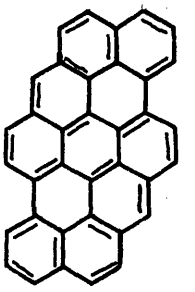
XXIII



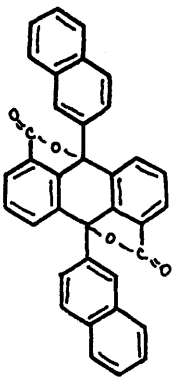
XXIV



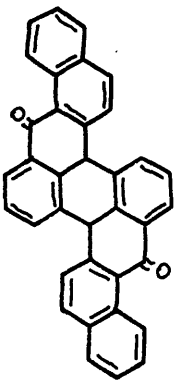
XXV



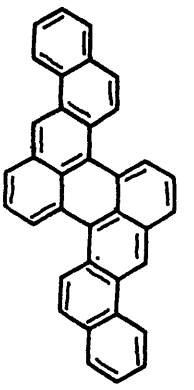
XXVI



XXVII



XXVIII

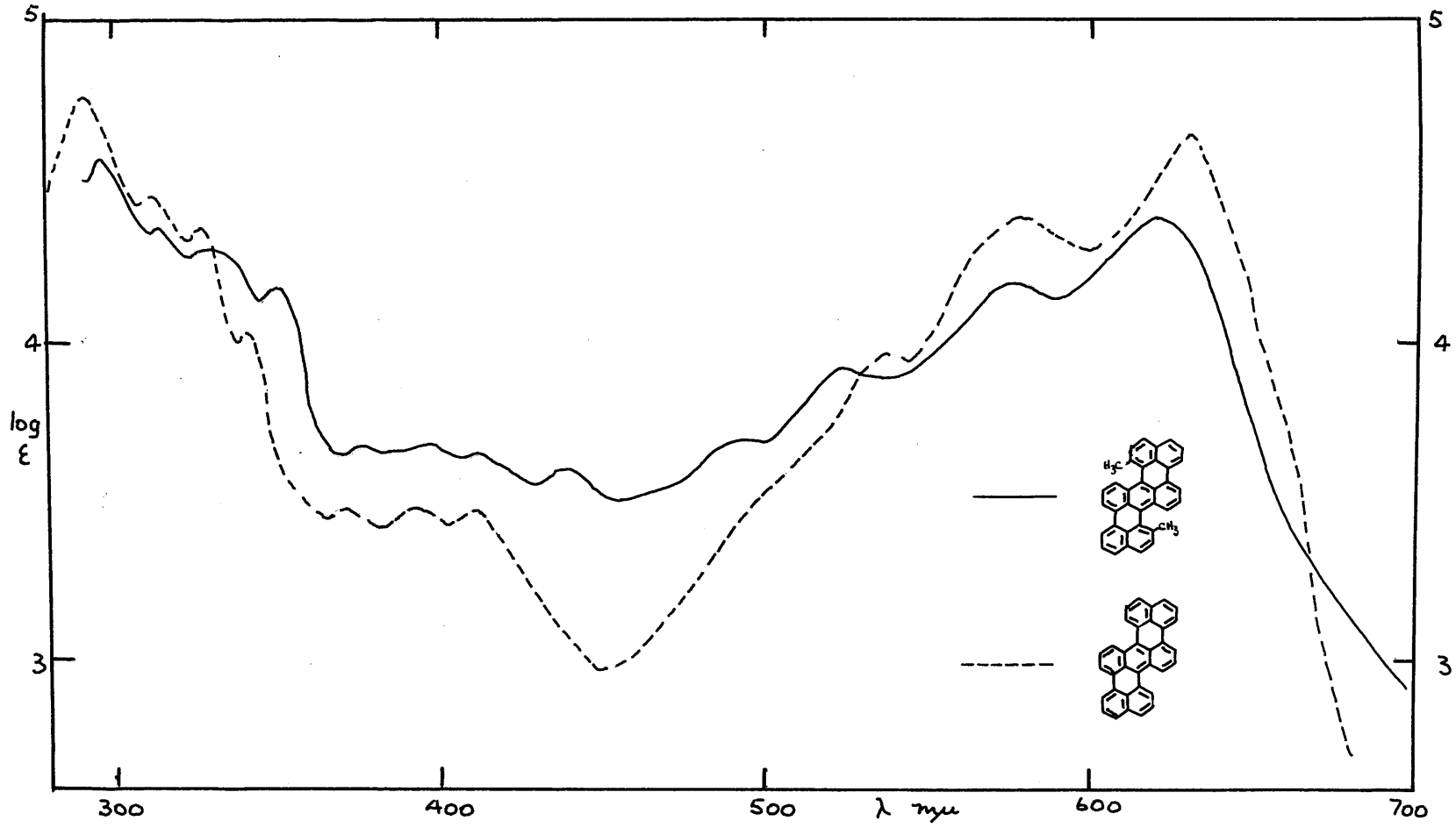


XXIX

The Synthesis of 3:4-5:6-10:11-12:13-Tetrabenzoperopyrene.

Although the structure of circumanthracene (XV) had been proved by X-ray crystallographic methods, an independent chemical synthesis of the compound was desirable. An obvious approach was to provide the carbon atoms 8 and 16 of circumanthracene by methyl substituents on the naphthyl nuclei of 1:5-dichloro-9:10-di-1'-naphthylanthracene (VIII). Although the synthesis of circumanthracene was not accomplished, the hydrocarbon 3:4-5:6-10:11-12:13-tetrabenzoperopyrene (XXVI) was prepared.

1:5-Dichloroanthraquinone reacted with 2-methyl-1-naphthylmagnesium bromide to give the diol (XXI) which was reduced to the corresponding anthracene (XXII) by boiling with hydriodic acid and acetic acid. When the latter was boiled with potassium hydroxide in quinoline for a short time, preferably in an inert atmosphere, 7':7''-dimethyl-1:9-5:10-diperinaphthyleneanthracene (XXIII) was obtained, mixed with monocyclised material, a benzoperylene derivative. The two compounds were separated by chromatography. The hydrocarbon (XXIII) has properties similar to the unmethylated hydrocarbon (IX), but (XXIII) is much more easily photo-oxidised than (IX). The spectra of the two hydrocarbons are given in Fig. 5. As expected, the two methyl groups cause a general flattening and a shift to the violet, of the spectrum of (IX). Methyl

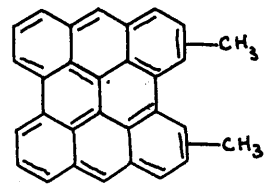


7':7"-Dimethyl-1:9-5:10-diperinaphthyleneanthracene (XXIII) in benzene. Maxima in mμ. 621, 578, 525; 439, 398, 378. 351, 332, 315; 296.

1:9-5:10-Diperinaphthyleneanthracene (IX) in benzene. Maxima in mμ. 630, 579, 536; 412, 392, 372; 342, 328, 312, 292.

Fig. 5

substituents in aromatic compounds have generally a weakly bathochromic effect, i.e. they cause a shift to the red. However, if the methyl groups are overcrowded, they exert a hypso-chromic effect (i.e. violet shift) which is sometimes quite large. It is interesting to compare the spectrum of 2:2'- and 3:3'-dimethylnaphthodianthrene (XXX) with the parent hydrocarbon (Brockmann and Randebrock (17), Brockmann (18)). The overcrowding by the methyl groups



XXX

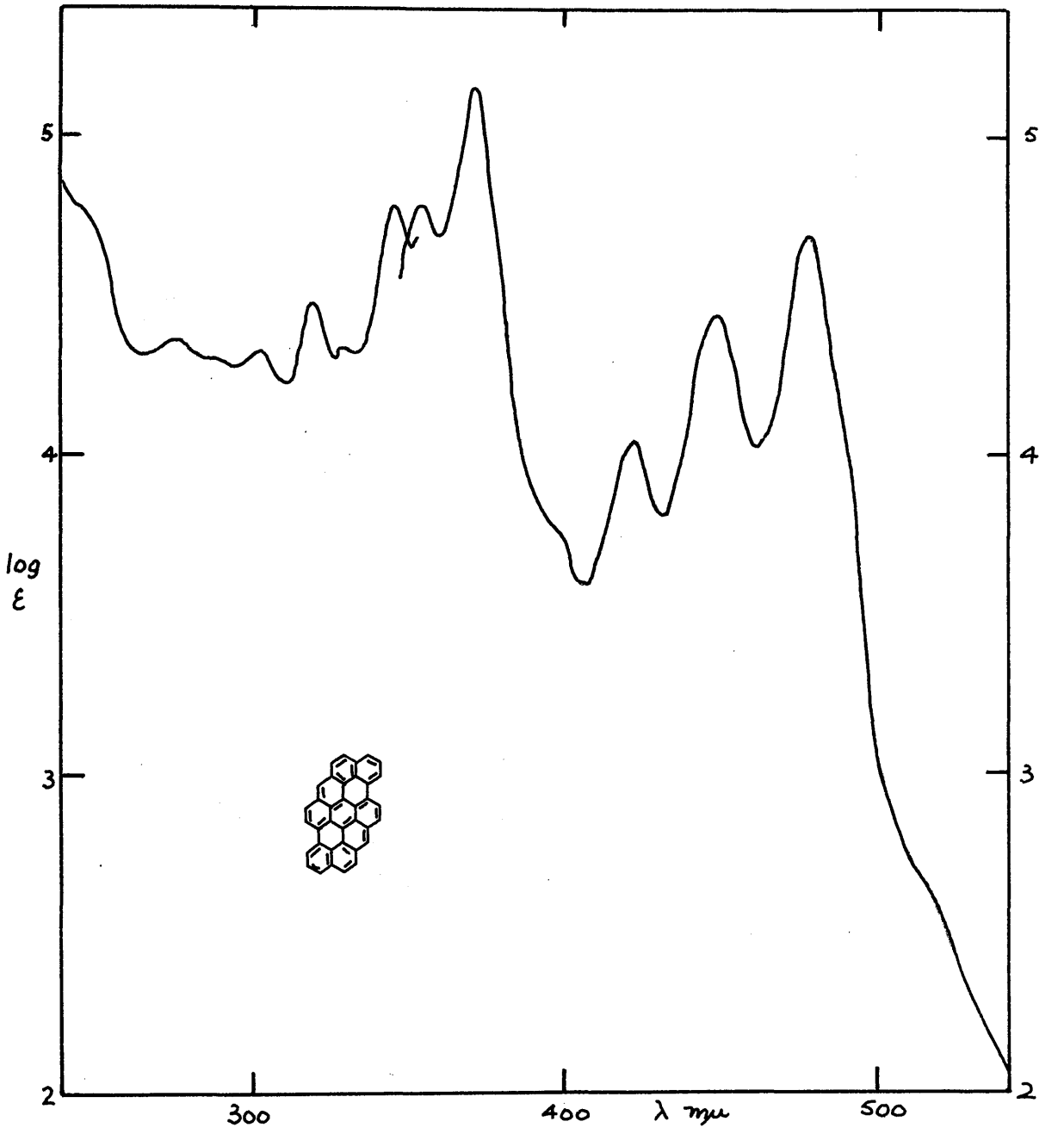
causes a distortion of the rings. Since the molecule is now no longer completely co-planar, a greater energy of activation is required and the molecule absorbs at lower wavelengths than the unmethylated hydrocarbon. The transitional probability is also likely to be decreased so that the intensity of the absorption bands will be reduced.

When 1:5-dichloro-9:10-di-(2'-methyl-1'-naphthylanthracene was heated for a longer time with potassium hydroxide and quinoline in the presence of air, the two methyl groups of the hydrocarbon also ring closed and the orange hydrocarbon 3:4-5:6-10:11-12:13-tetrabenzoperopyrene (XXVI) was obtained. A small quantity of a red, very soluble mixture

of compounds which would not be separated or identified, was also obtained. The yield of the tetrabenzoperopyrene was very low, and a variety of methods and condensing agents were tried, but with no improvement in the yield.

The spectrum of the tetrabenzoperopyrene is given in Fig. 6. The very strong violet shift of the long wave bands, caused by the formation of the two new rings, is obvious when the spectrum of tetrabenzoperopyrene is compared with those of the hydrocarbons (IX) and (XXIII) (Fig. 6). The very strong hypsochromic effect of the two CH groups in positions 7 and 14 compares very strikingly with the large bathochromic effect of oxido groups in the same positions (see Fig. 7).

Scholl and Meyer (19) claimed to have prepared a dinaphthocoronene, which has the same structural formula as the tetrabenzoperopyrene, but the properties of the two hydrocarbons are not identical. Although the above synthesis almost certainly leads to the tetrabenzoperopyrene structure, the synthesis of the dinaphthocoronene begins with an ambiguous condensation. Scholl, Meyer and Winkler (20) assumed that condensation of anthraquinone-1:5-dicarboxylic acid pseudo-chloride with naphthalene under the influence of aluminium chloride in nitrobenzene would give the di-α-naphthyl-dilactone (XXIV), but they did not prove this. Baddeley (21) has shown that naphthalene



3:4-5:6-10:11-12:13-Tetrabenzoperopyrene (XXVI). Maxima in mμ. 478, 449, 422; 371.5, 354, in 1-methylnaphthalene; 346, 320, 302, 275 in dioxan.

Fig. 6.

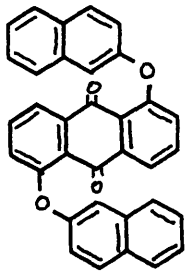
reacts in the β position in Friedel-Crafts reactions when nitrobenzene is used as solvent, so that Scholl's product was probably the di-β-naphthyl-dilactone (XXVII).

Cyclisation of the dilactone (XXVII) would yield only the dinaphthoperylenequinone (XXVIII) whereas the α-derivative (XXIV) would give, first, an isomeric dinaphthoperylene-quinone (XXV) and then dinaphthocoronenequinone. Scholl and Meyer (19) claimed to have obtained the two latter quinones, but reported that there was apparently no difference in their properties. Also, changes in the conditions of cyclisation, such as longer treatment with the cyclising agent, which would be expected to lead to higher yields of the dinaphthocoronenequinone, apparently did not do so. It is suggested that they were actually the same compound, the dinaphthoperylenequinone (XXVIII). Reduction and dehydrogenation of this quinone could yield the dinaphthperylene (XXIX). The reported properties of Scholl and Meyer's hydrocarbon are compatible with the structure (XXIX).

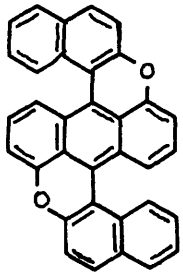
When coronene is prepared by hydrogenation of coal a more highly condensed hydrocarbon is obtained as a by-product which Fromherz, Thaler and Wolf (22) considered to be identical with Scholl and Meyer's hydrocarbon. They did not report a direct comparison of the two hydrocarbons.

The absorption spectrum of the hydrocarbon of Fromherz et al. is quite different from the spectrum of (XXVI) (Fig. 6). Therefore their hydrocarbon must have some other structure.

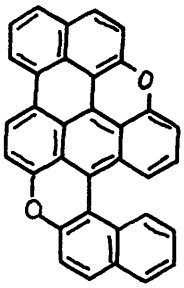
Unfortunately the sensitivity of the dimethyl diperinaphthyleneanthracene and the low yields of tetrabenzoperopyrene did not allow the investigation of possible routes to circumanthracene from these compounds.



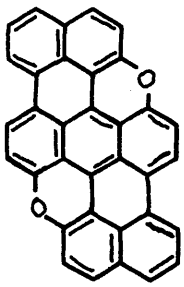
XXXI



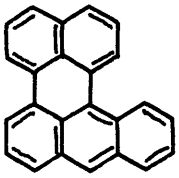
XXXII



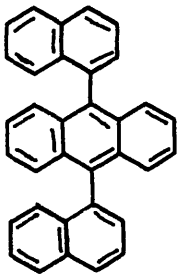
XXXIII



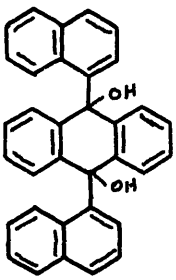
XXXVI



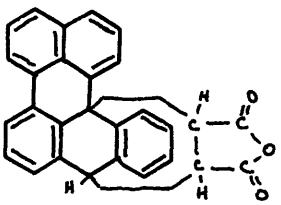
XXXV



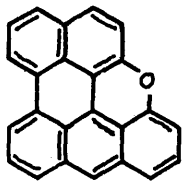
XXXIV



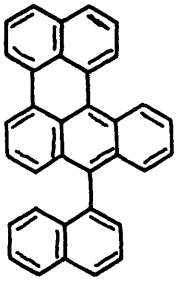
XXXVII



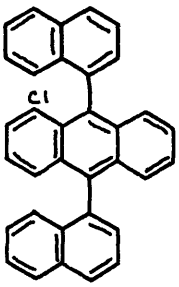
XXXVIII



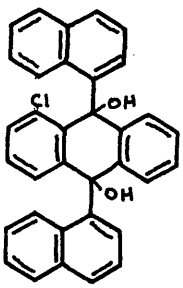
XXXIX



XL



XLI



XLII

The Synthesis of 1:2-Benzoperylene.

Clar and Stewart (23) attempted to synthesise 1:9-5:10-diperinaphthyleneanthracene (IX) from the dioxido-diperinaphthyleneanthracene (XXXVI). Reduction of the dioxido compound and dehydrogenation of the product gave a red hydrocarbon which was thought to be diperinaphthyleneanthracene. Further study of the properties of this hydrocarbon by the present author showed that it was not diperinaphthyleneanthracene, but probably 1:2-benzoperylene (XXXV). The structure of the dioxido compound (XXXVI) was therefore re-examined, and, since previous syntheses (24, 25) of benzoperylene had not sufficiently characterised the compound, a new synthesis of this hydrocarbon was accomplished.

Stewart (23) had shown that when 1:5-di-2'-naphthyloxyanthraquinone, prepared from β-naphthol and 1:5-dichloroanthraquinone was heated in an aluminium chloride-sodium chloride melt at 180° for 10 minutes and at 145° for 15 minutes, two compounds were obtained. The lower melting, more soluble of the two, a red compound, could be converted into the other compound, which was blue, by further treatment with aluminium chloride. Therefore the two compounds were considered to be the dioxido-dinaphthylanthracene (XXXII) and the dioxido-diperinaphthyleneanthracene (XXXVI) respectively.

When the dinaphthyloxyanthraquinone (XXXI) was heated with aluminium chloride at 180° for 35 minutes, no red compound was obtained and the reaction product, after extraction of the blue compound with hot xylene, was found to contain a green compound, which was separated by extraction with boiling 1:2:4-trichlorobenzene and by sublimation. This compound which had a very high melting point and a very low solubility is almost certainly the fully condensed dioxido compound (XXXVI), so that the blue compound must be the partially ring closed dioxido-naphthylbenzoperylene (XXXIII). That the structures assigned to the three compounds (XXXII), (XXXIII) and (XXXVI) are correct is confirmed when the spectra of the three compounds are examined together (Fig. 7). The shapes of the long wave-band systems are very similar and each ring closure produces a strong red shift of the first group of bands, whilst the intense band near 300 mμ remains relatively unaltered.

The formation of 1:2-benzoperylene (XXXV) from the blue compound (XXXIII) must result from fission of the naphthyl group, either during reduction of the dioxido compound with red phosphorus and hydriodic acid under pressure or during dehydrogenation of the reduced product with palladium charcoal.

Clar (24) had synthesised 1:2-benzoperylene by reduct-

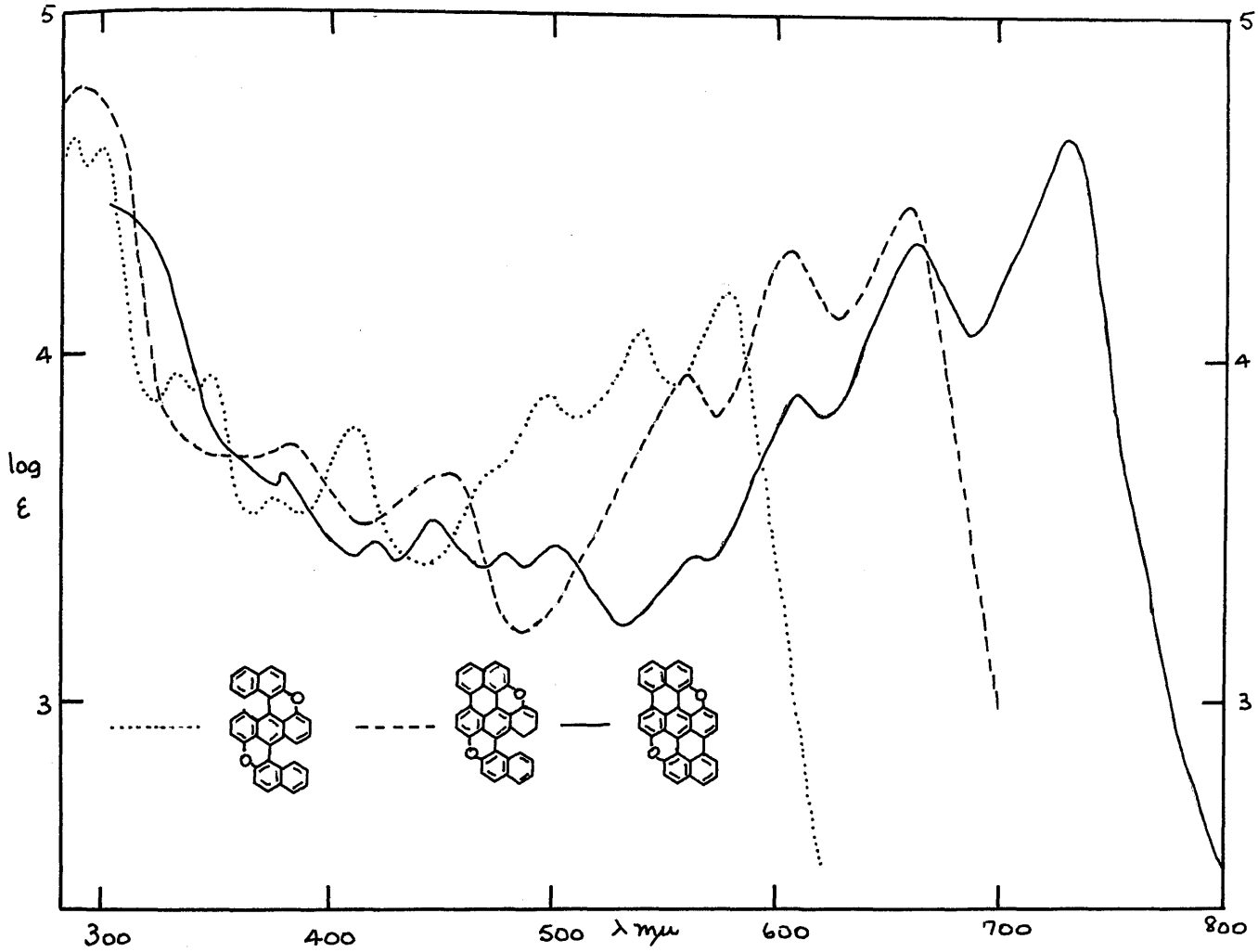
Fig. 4

done

twice.

cut one

out.



1:2'-5:2"-Dioxido-9:10-di-α-naphthylanthracene (XXXII) in benzene. Maxima in mμ. 576, 537, 495; 409, 384, 347, 331; 299, 286.

4:2'-12:1"-Dioxido-3-1'-naphthyl-1:2-benzoperylene (XXXIII) in benzene. Maxima in mμ. 660, 605, 560, 455, 394; 290.

4:2'-8:2"-Dioxido-1:9-5:10-diperinaphthyleneanthracene (XXXVI) in 1:2:4-trichlorobenzene. Maxima in mμ. 732, 663, 610; 500; 445, 421, 380.

Fig. 7.

-ion of 1:2-benzoperylene-3:10-quinone, but he was unable to crystallise the hydrocarbon. A compound supposed to be benzoperylene was isolated by Clar and Wright (25) after the treatment of 9:10-di-1'-naphthyl-9:10-dihydro-anthracene-9:10-diol (XXXVII) in an aluminium chloride-sodium chloride melt at 110°. Apart from its spectrum, this compound was not fully characterised and the authors did not exclude the possibility that the compound might be the 3-naphthyl-1:2-benzoperylene (XL). As will be shown below, this was in fact the case.

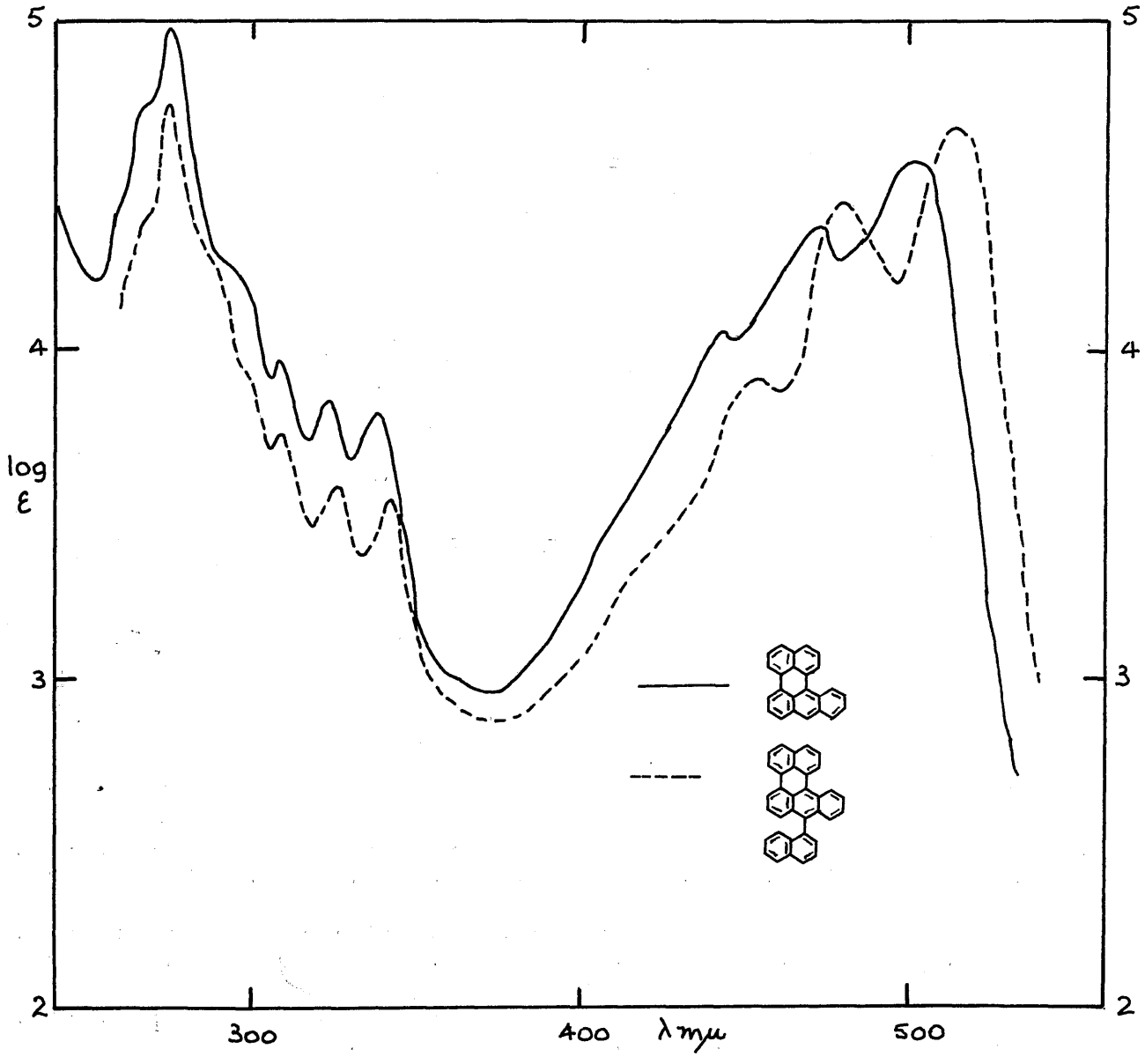
The work of Wright was repeated but the diol (XXXVII) was first reduced to the dinaphthylanthracene (XXXIV) before ring closure. In order to ensure that the naphthyl group was split off, the melt was heated to a high temperature. 9:10-Dinaphthyl-9:10-dihydroanthracene-9:10-diol (XXXVII) was prepared by the reaction of anthraquinone and naphthyllithium. The yield of the diol, by this method, was higher than those reported, using the Grignard reagent, naphthylmagnesium bromide (6, 7, 11). Reduction of the diol by boiling with acetic acid and potassium iodide (26) gave 9:10-dinaphthylanthracene (XXXIV), which was then heated to 160°C in an aluminium chloride-sodium chloride melt. The main product of the reaction was 1:9-4:10-diperinaphthyleneanthracene (II), but anthracene, perylene and 1:2-benzoperylene were distilled from the reaction

product. The perylene is formed by the re-combination of naphthyl groups split off during the reaction. The separation of perylene and benzoperylene was difficult and, until the benzoperylene was completely free of perylene, it could not be crystallised. The two compounds were eventually separated by very slow fractional sublimation in vacuum in a stream of carbon dioxide.

1:2-Benzoperylene prepared in this way was identical with the red hydrocarbon obtained from the blue dioxido compound (XXXIII) and the visible band maxima of the absorption spectrum were also the same as those of the non-crystalline hydrocarbon obtained by Clar (24). It was, however, different from the hydrocarbon obtained by Wright, although, as seen in Fig. 8, the absorption spectra of the two compounds are very similar. As would be expected, the naphthyl substituent had a small bathochromic effect on the spectrum of benzoperylene.

Benzoperylene is rather quickly photo-oxidised and reacts rapidly with maleic anhydride to give an adduct (XXXVIII). Comparison of the spectrum of the latter with that of benzoanthrene, (Fig. 9) (14) confirms that the structure of the adduct (XXXVIII) is as assigned.

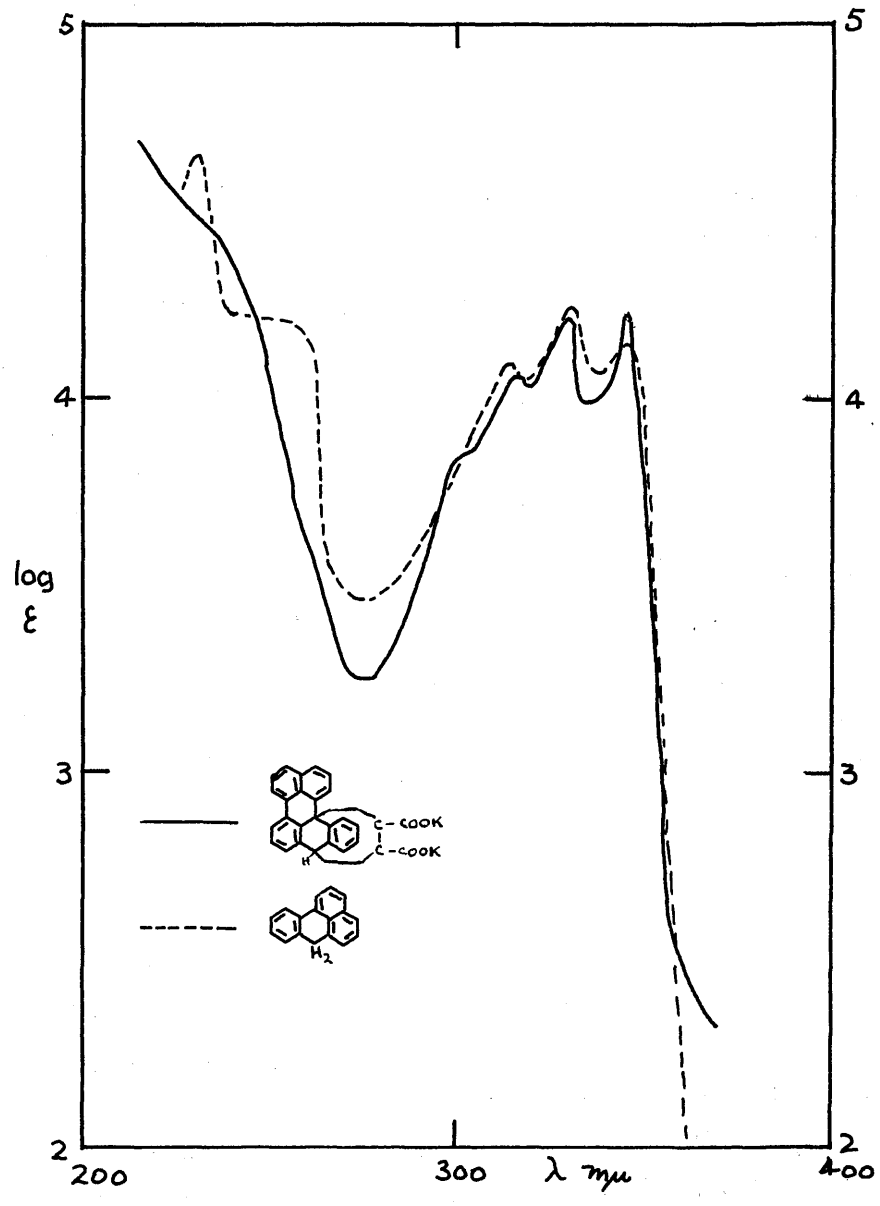
In order to confirm that the hydrocarbon obtained by Wright from the diol (XXXVII) was naphthyl-benzoperylene, this hydrocarbon was prepared by a method analogous to



1:2-Benzoperylene (XXXV) in alcohol. Maxima: 503, 473, 445; 339, 323, 308; 276.

3-1'-Naphthyl-1:2-benzoperylene (XL) in hexane. Maxima: 514, 480, 454; 342, 326, 310; 276.

Fig. 8.



Dipotassium salt from the maleic anhydride adduct (XXXVIII) in water. Maxima: 345, 329, 314.

Benzanthrene in alcohol. Maxima: 344, 329, 312; 250; 228.

Fig. 9.

that used in the synthesis of 1:9-5:10-diperinaphthylene-anthracene.

The diol (XLII), obtained from 1-chloro-anthraquinone and 1-naphthylmagnesium bromide, was reduced to 1-chloro-9:10-dinaphthylanthracene (XLI) with acetic acid and hydriodic acid. This ring closed very readily when boiled with quinoline and potassium hydroxide to give the naphthyl benzoperylene (XL). It was identical with the hydrocarbon obtained from the diol (XXXVII). The molecular weight of the two hydrocarbons (XXXV) and (XL), by the Rast method, is in agreement with the assigned structures.

It is noteworthy that the difference of $\sqrt{\lambda}$ between 1:2-benzoperylene (XXXV) and 12:1'-oxido-1:2-benzoperylene (XXXIX) (27) is equal to the difference between 1:9-5:10-diperinaphthyleneanthracene (IX) and the dioxido compound (XXXVI).

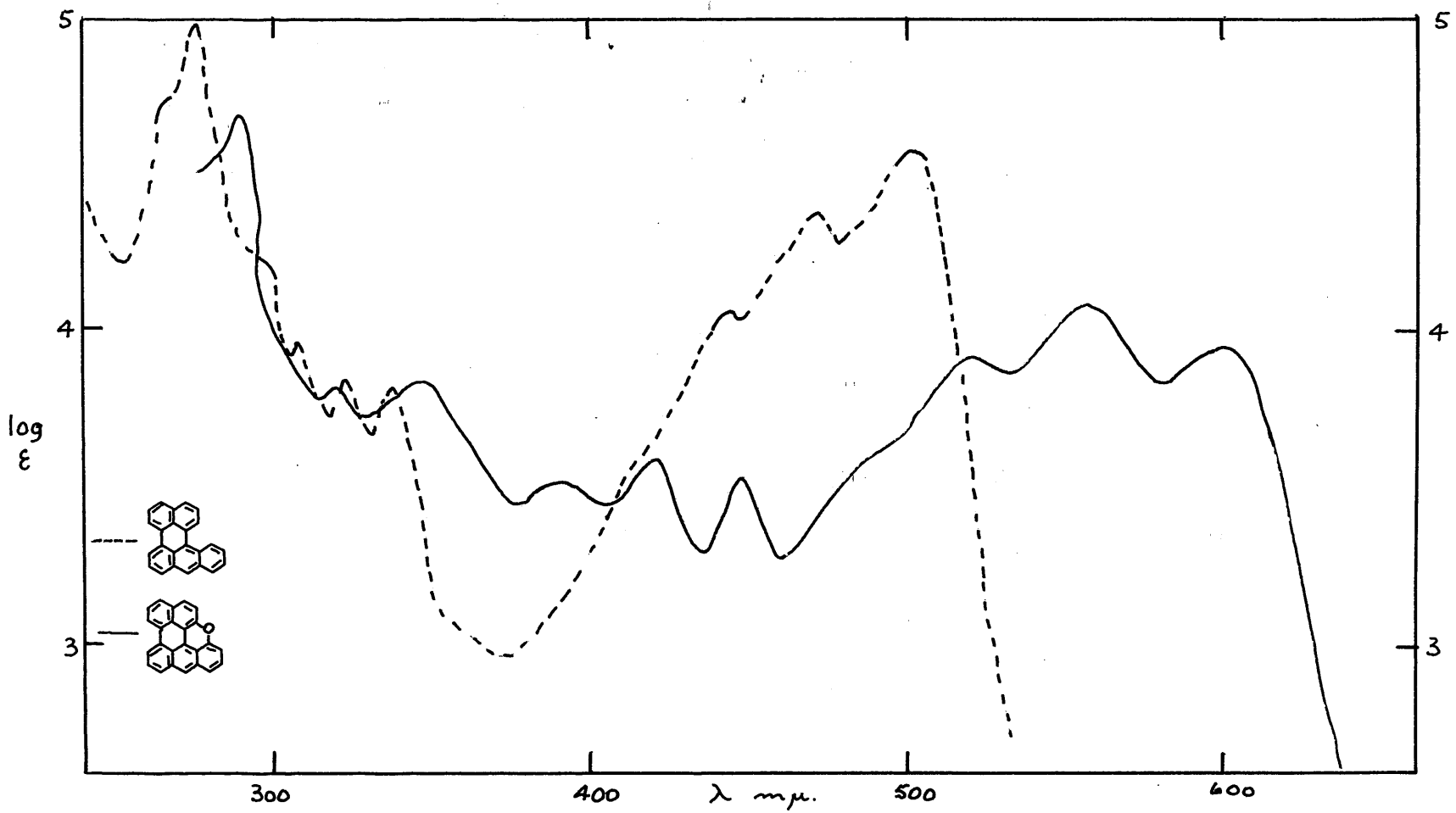
i.e. $\sqrt{\lambda}_{XXXIX} - \sqrt{\lambda}_{XXXV} = \sqrt{\lambda}_{XXXVI} - \sqrt{\lambda}_{IX}$

In benzene (mμ), except XXXVI which is in trichlorobenzene

$$\sqrt{599} - \sqrt{511} = 2 = \sqrt{732} - \sqrt{630}$$

This indicates that the anellation principle also applies to the above cases where oxygen-containing rings are involved.

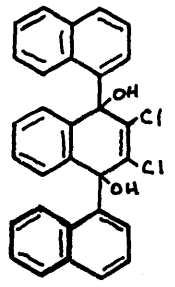
The spectrum of oxidobenzoperylene (XXXIX) is given in Fig. 10 with that of benzoperylene for comparison.



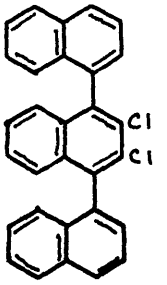
12:1'-Oxido-1:2-benzoperylene (XXXIX) in benzene. Maxima: 599, 555, 521; 446, 420, 345, 319; 289.

1:2-Benzoperylene (XXXV) in alcohol. Maxima: 503, 473, 445; 339, 323, 308; 276.

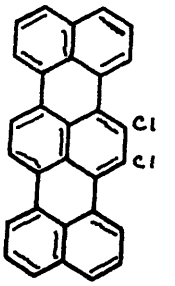
Fig. 10



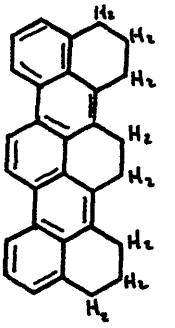
XLIII



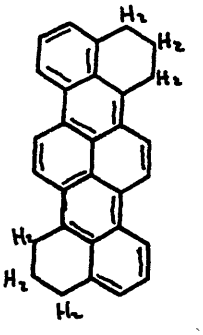
XLIV



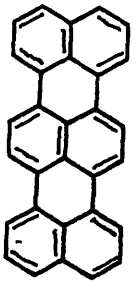
XLV



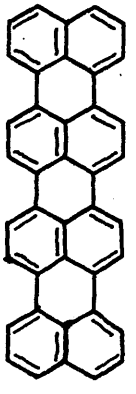
XLVIII



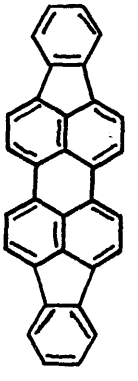
XLVII



XLVI



XLIX



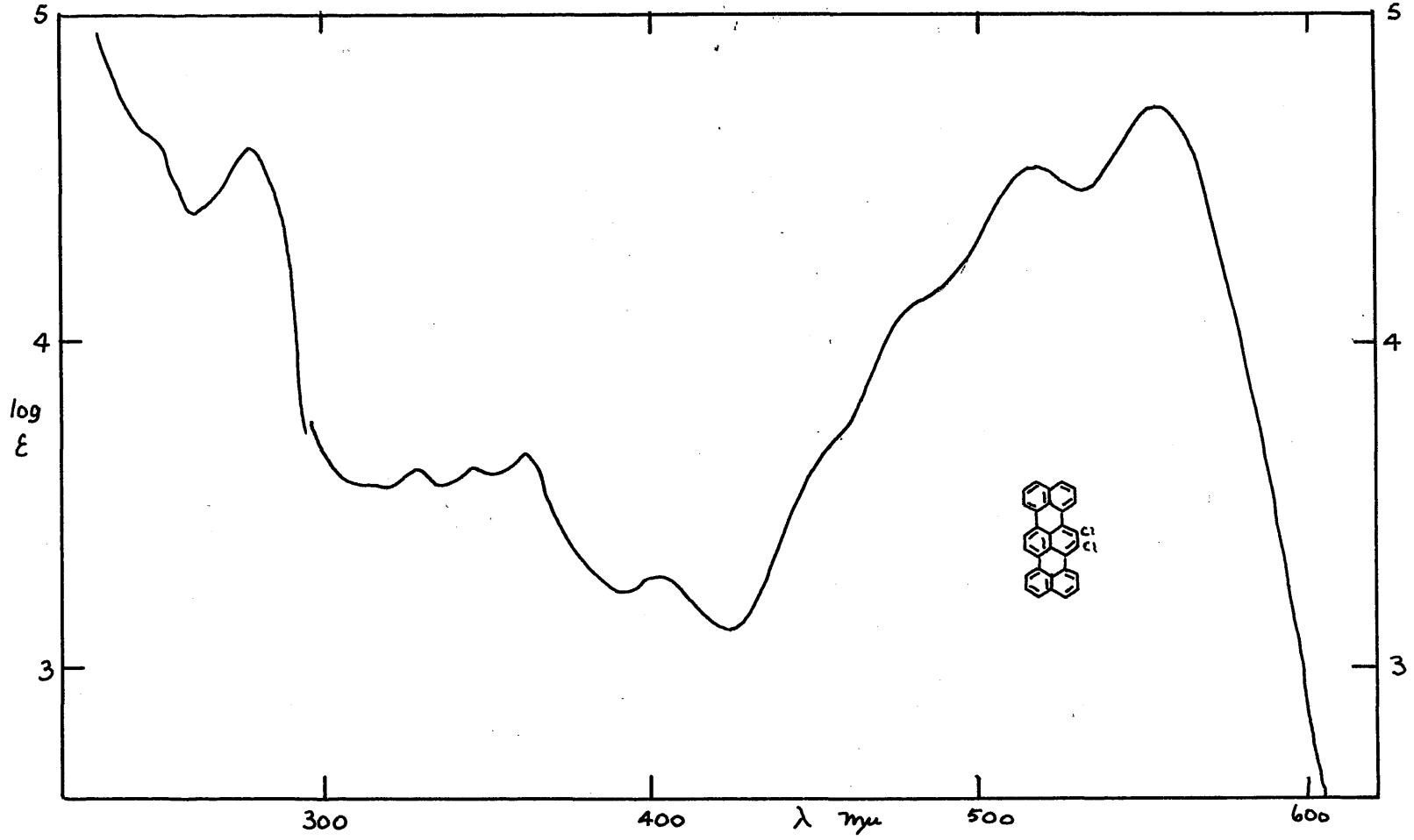
L

Syntheses of Terrylene and Quaterrylene.

Clar (28) isolated a hydrocarbon which he considered to be terrylene (XLVI), from the reaction of perylene and 1-bromonaphthalene in a sodium chloride-aluminium chloride melt at 130°. He also obtained as a by-product, a compound which was thought to be a dibromoterrylene although, beyond the fact that is gave a positive Beilstein test, the compound was not fully analysed. Although the properties of Clar's hydrocarbon appeared to be in agreement with the structure of (XLVI) it was felt that a less ambiguous synthesis of the hydrocarbon was desirable, and, with the assistance of Mr. R.M. Laird in the early stages, the following synthesis was carried out.

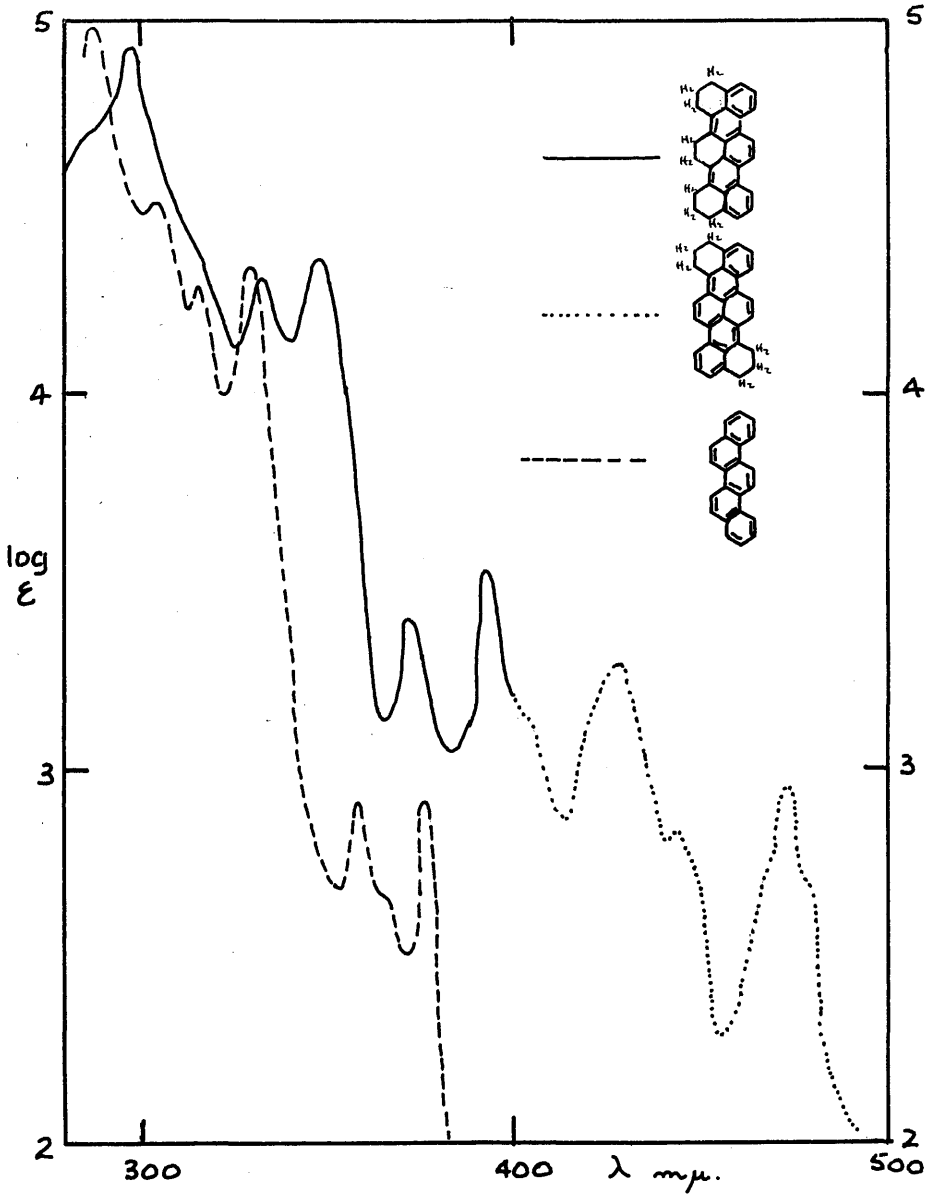
2:3-Dichloro-1:4-naphthoquinone was condensed with naphthylmagnesium bromide to give the diol (XLIII) as described by Clar and Engler (29). Reduction of the diol by heating with hydriodic acid in acetic acid gave 2:3-dichloro-1:4-di-1'-naphthylnaphthalene (XLIV) which was condensed by heating at 115° in a sodium chloride-aluminium chloride melt. Chromatography of the reaction product, either at room temperature or, more easily at 120°, gave 7:8-dichloro terrylene (XLV) as dark purplish needles and in addition small amounts of two other substances; first, perylene which was formed by the re-combination of

naphthyl radicals split off during the condensation. Second, an orange hydrocarbon, m.p. 434-436. This compound was found to be identical with Clar's hydrocarbon terrylene. At first sight, this seemed to suggest that the structure of Clar's hydrocarbon was correct, since it was quite feasible that chlorine atoms could be removed, either from (XLIV) or (XLV), by the hydrogen liberated during ring closure (cf. the formation of a small quantity of anthracene during the ring closure of (IV) with aluminium chloride). However, only the structure of the dichloro-terrylene (XLV) is certain and proof of the structure of terrylene (XLVI) must depend on the dechlorination of (XLV). This was done by reduction of (XLV) with hydriodic acid and red phosphorus in a sealed tube at 210°. Analysis of the product indicated that it was octahydroterrylene. The close relationship of the spectrum of the compound with that of picene (Fig. 12) shows that the octahydroterrylene has almost certainly the structure (XLVIII). The spectrum of the reduction product also shows weaker bands at 474, 443 and 426 mμ, which are probably due to a small proportion (~2%) of a less highly hydrogenated compound, most likely the dibenzopyrene derivative (XLVII), mixed with the octahydroterrylene. A small quantity of a deep purplish hydrocarbon was also obtained from the reduction.



7:8-Dichloroterrylene (XLV). Maxima: 556, 518; 402, 362, 346, 327.5, 313 in benzene; 278 in dioxan.

FIg. 11

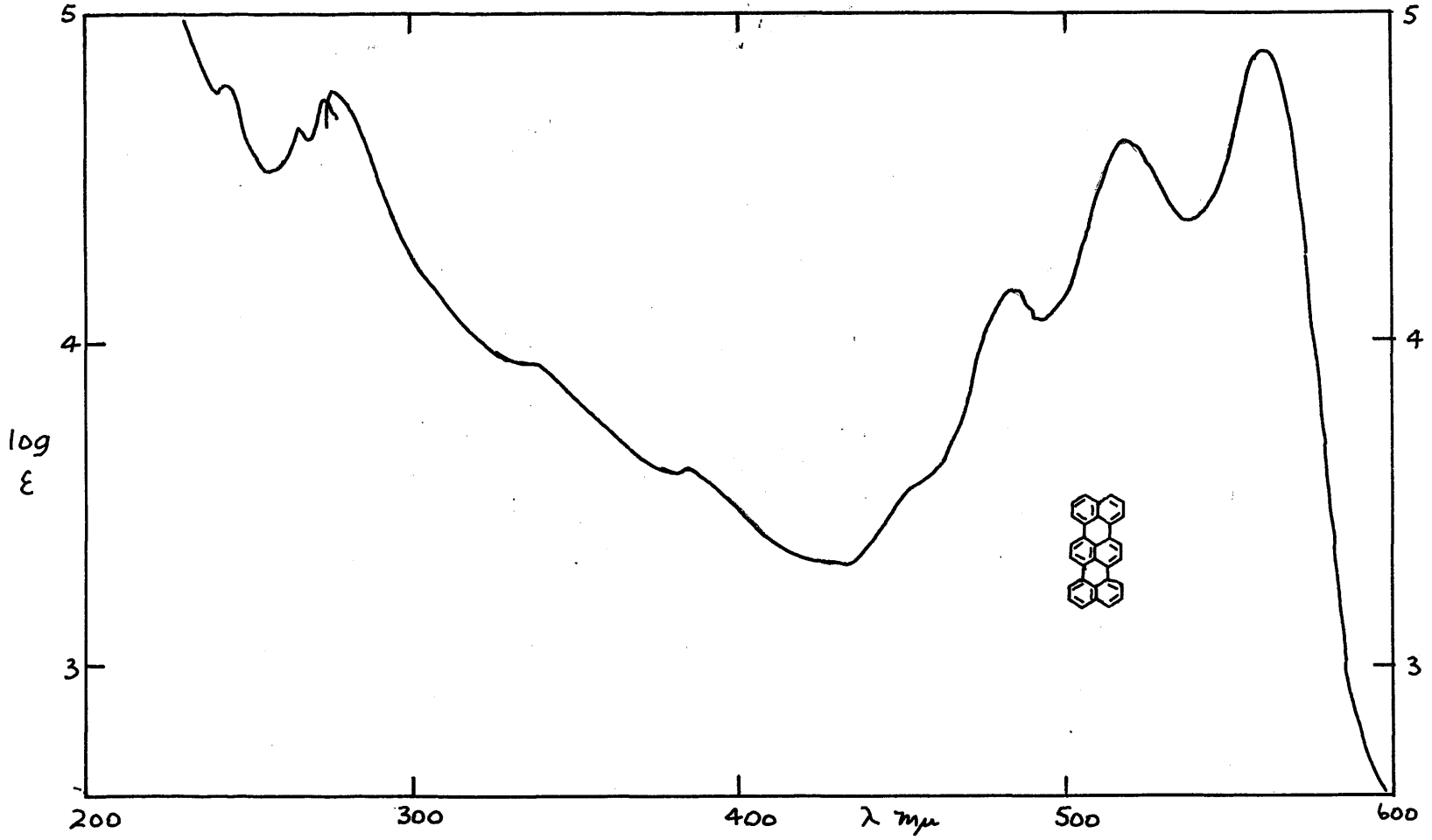


Octahydroterrylene (XLVIII) in benzene. Maxima: 393, 372; 348, 333; 298.

Hexahydroterrylene (XLVII) in benzene. Maxima: 474, 443, 428.

Picene in benzene. Maxima: 376, 358; 329, 315, 304; 281.

Fig. 12.



Terrylene (XLVI). Maxima: 560, 518, 485; 275 in benzene; 274, 265, 244 in dioxan.

Fig. 13

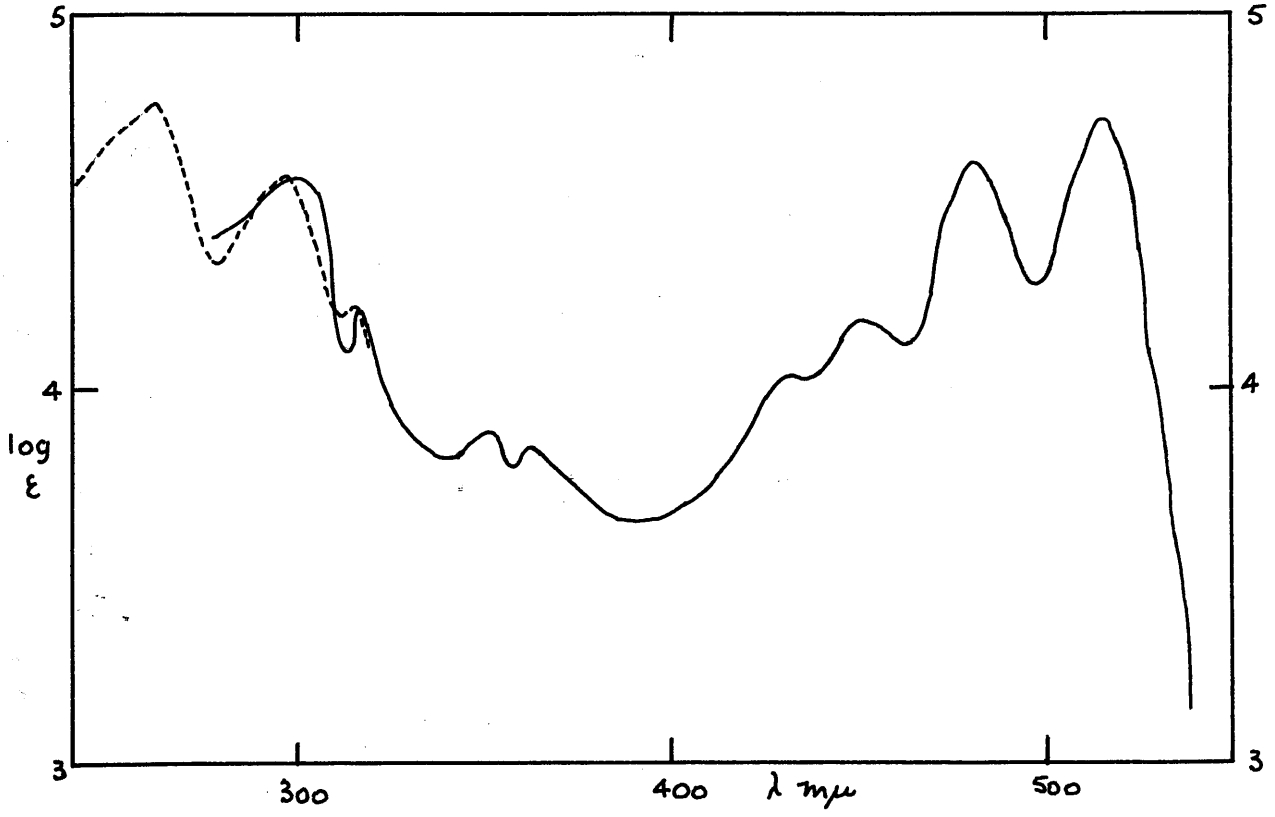
The vapour-phase dehydrogenation of the octahydroterrylene by sublimation under vacuum in a stream of carbon dioxide through granular 20% palladium charcoal (prepared according to (30), (31), at 380° gave a single compound, a deep purplish hydrocarbon which must be terrylene (XLVI). It was identical with the purple by-product of the above hydriodic acid reduction, so that some terrylene must also be formed with the octahydroterrylene. The spectrum of terrylene, which is given in Fig. 13, is seen to be rather similar to the spectrum of dichloroterrylene (XLV) (Fig. 11). The two chlorine atoms have only a slight hypsochromic effect (4 mμ). The spectrum of (XLVI) was observed to be very similar to that of the compound regarded as dibromo-terrylene by Clar (28). This compound was analysed and found to contain only a small percentage of bromine, so that any mono- or dibromoterrylene is present as an impurity in what is mainly terrylene. This would account for the low melting point reported by Clar, 447-450°, compared to 510-511° of pure terrylene. The similarity between the spectra of dichloroterrylene and terrylene (Figs. 11 and 13) also suggests that the presence of a small quantity of bromo or dibromoterrylene in terrylene could not be detected in the absorption spectrum.

The hydrocarbon with the first band at 560 mμ from the condensation of perylene and bromonaphthalene was later purified by Zinke, Nussmüller and Ott (32). The spectrum of their compound is almost identical with the spectrum of terrylene, Fig. 13, obtained from dichloroterrylene. The other reported properties are similar, though a comparison of melting points are not possible, since they only report that the compound did not melt below 470°.

The fact that the same compound is obtained from the condensation of perylene and bromonaphthalene as well as from the above synthesis, provides further confirmation that the hydrocarbon with the first band at 560 mμ has the structure (XLVI).

The structure of the orange hydrocarbon with the first band at 516 mμ, the spectrum of which is given in Fig. 14, is still unknown.

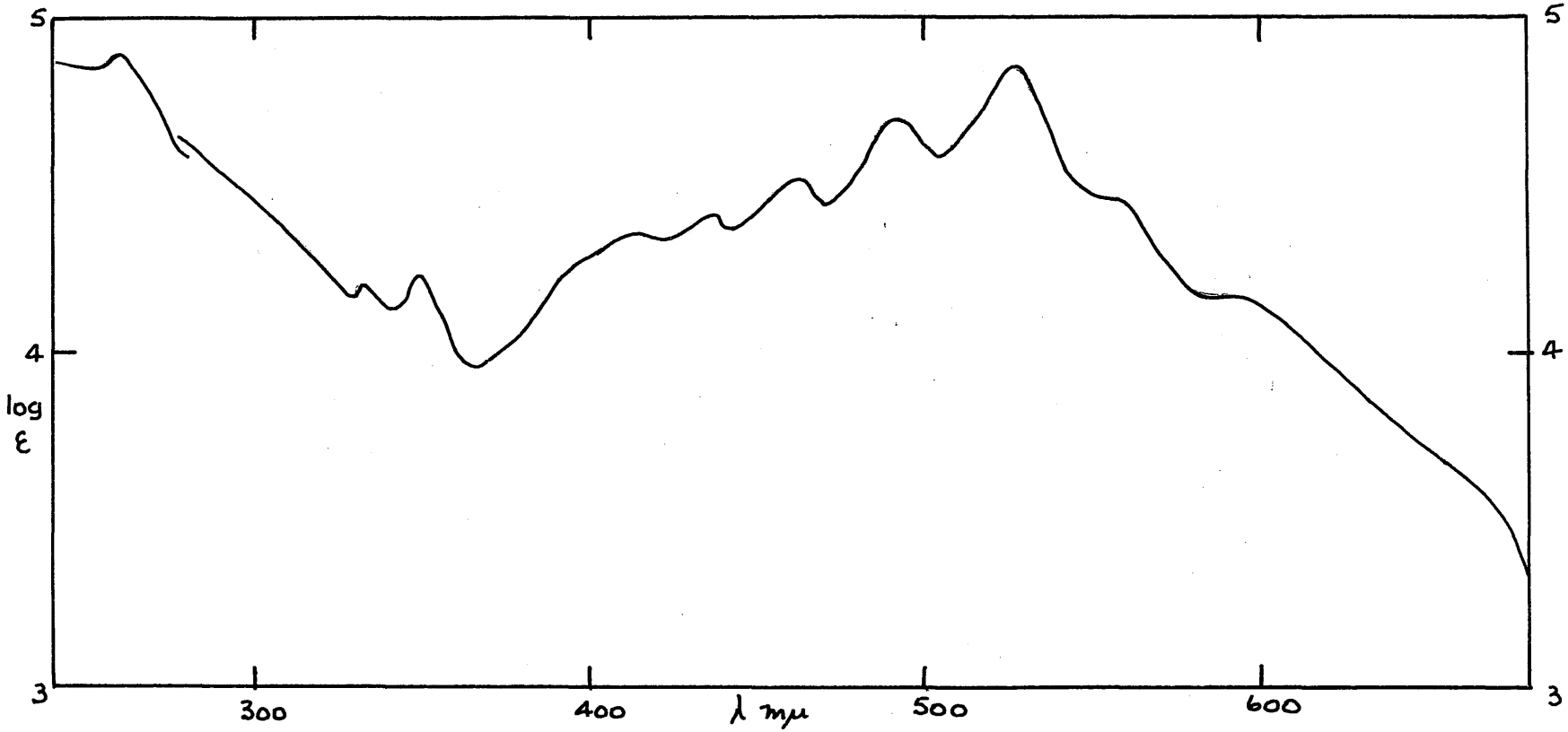
When Zinke, et al. (32) repeated the condensation of perylene and bromonaphthalene, they obtained the same two hydrocarbons (first bands at 516 and 560 mμ) as Clar (28). They claimed to obtain the latter hydrocarbon from the condensation of naphthalene with 3:9-dibromoperylene, 3:4-9:10-tetrachloroperylene and perylene respectively, and of perylene itself, therefore they assigned the structure quaterrylene (XLIX) to the hydrocarbon.



By-product from preparation of dichloroterrylene. ("Terrylene" of E. Clar). Maxima: 516, 483, 453; 365, 352, 318, 301, in benzene; 316, 298, 262 in dioxan.

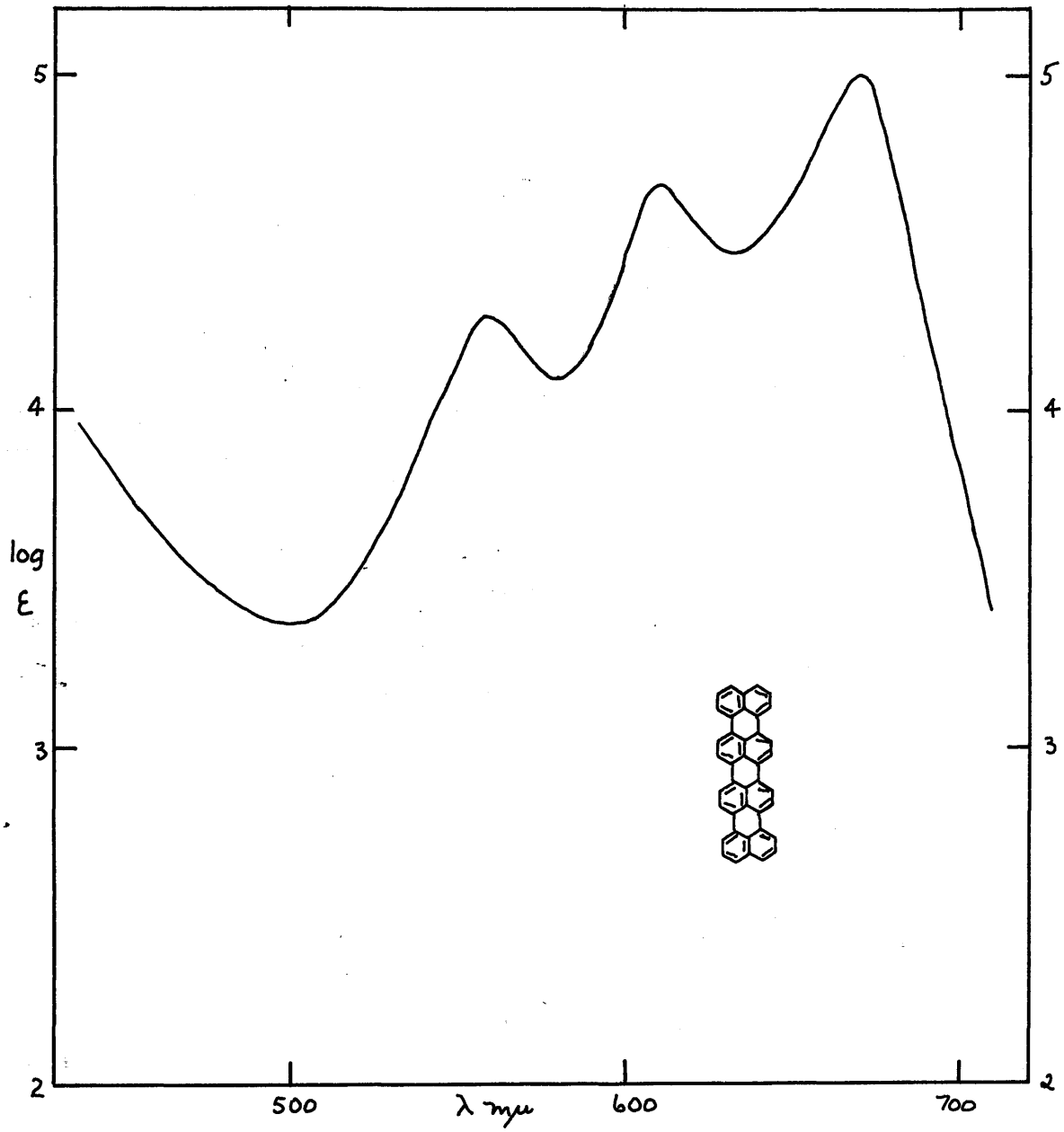
Fig. 14.

A synthesis of quaterrylene had been described by Clar (28), by the action of aluminium chloride on perylene in benzene as solvent. Zinke, Pack, Ott and Weisenberg (33) later showed that perylene, rather than condense with itself, had reacted with two molecules of the solvent, benzene, to give periflanthene (L). Since the condensation of perylene still seemed the most direct route to the hydrocarbon (XLIX), the reaction was repeated by the present author using a sodium chloride-aluminium chloride melt, instead of benzene as the reaction medium. The condensation was repeated several times over a range of 120-150°, but no hydrocarbon with the first band at 560 mu was ever detected. Apart from unreacted perylene, two other hydrocarbons were isolated by sublimation under vacuum from the reaction mixture. First, a reddish-brown hydrocarbon (m.p. 467-469°) sublimed at 400°. Its absorption bands are at 527, 493 and 461 mμ in benzene (Fig. 15). At a considerably higher temperature a blue hydrocarbon with a green sheen sublimed. It was completely insoluble at room temperature and even in boiling 1-methyl-naphthalene it was only slightly soluble. It dissolved readily in boiling pyrene (b.p. 404°) and crystallised in large green plates which did not melt below 570°. Since the solubility of this hydrocarbon was so low, its absorption spectrum could not be satisfactorily measured at



By-product from preparation of Quaterrylene. Maxima: 527, 495, 461, 436, 413; 351, 335, in benzene; 259 in dioxan.

Fig. 19



Quaterrylene (XLIX). Maxima: 670, 610, 558 in 1-methylnaphthalene at 150°. At room temperature: 673, 615, 563.

Fig. 16.

room temperature. Fig. 16 shows the spectrum measured at 150°. The intensities are only qualitative.

The analyses of both hydrocarbons satisfy the structure of quaterrylene, but only the blue hydrocarbon has the properties to be expected of such a structure. The melting point of the reddish brown hydrocarbon is lower than that of terrylene, and absorbs at a lower wavelength than the latter.

	Melting Point.	1st p-Band of Spectrum in Benzene mμ.
Naphthalene	80°	287
Perylene	274°	439
Terrylene	511°	560
Blue hydrocarbon	>570°	673
Reddish-brown hydrocarbon	467°	527

The blue hydrocarbon therefore is almost certainly quaterrylene. The structure of the reddish-brown hydrocarbon is still unknown.

It is difficult to assess the significance of the results of Zinke et al. (32) since no yields are reported for their condensations. They do not indicate whether the hydrocarbon with the first band at 560 mμ was the only, or even the major product of the reaction. Since they did not have a melting point of the hydrocarbon they could

not make a direct comparison of melting points between the products of the various reactions. A possible product or intermediate in the condensation of naphthalene and the halogenated perylenes would be halogenated terrylenes. The spectra of terrylene and dichloroterrylene are rather similar so that it may be difficult to distinguish spectroscopically between terrylene and other halogenated terrylenes. It is also possible that the halogen is removed by hydrogen liberated during ring closure. Their claim to have obtained the hydrocarbon (first band at 560 mμ), at least in significant yield, from the condensation of perylene alone has been shown to be open to doubt.

It had previously been thought that the p-bands of the polyrylenes, i.e. naphthalene, perylene, terrylene, etc., behaved in a similar manner to the p-bands of the polyphenyls, i.e. they followed the Condensation Principle (28, 34). In the acene series the $\sqrt{\lambda}$ p of the first bands are proportional to 6, 7, 8, 9, 10 and 11, but in the polyphenyls, as the series is ascended from benzene to sexiphenyl, each shift to the red is less than the preceding shift. In fact, the difference between the first p-bands are halved from member to member, giving a converging, infinite geometrical series. The frequency ν_n of the n^{th} member can be

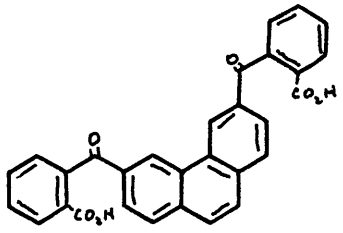
calculated from the equation

$$\nu_n = \nu_1 - d_1 \left(\frac{1-q^n}{1-q}\right)$$

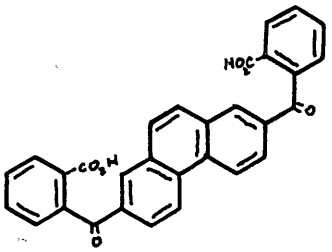
where ν_1 is the frequency of the first member of the series (benzene), d, the difference between the 1st and 2nd members and $q = \frac{1}{2}$ for the polyphenyl series. When terrylene was thought to be the hydrocarbon with the 1st band at 516 (Clar (28)), the first p-bands of naphthalene, perylene and terrylene appeared to agree with the above formula, except that in this case $q = \frac{1}{4}$, i.e. the difference of the first p-bands decrease 4-fold from member to member. However, with the discovery that terrylene absorbs at 560 mμ, and quaterrylene at 673 mμ, it is obvious that the polyrylenes form a normal anellation series.

	Perylene	Terrylene	Quaterrylene
λ in mμ	439	560	673
R_p (cm.$^{-1}$)	147×10^4	147×10^4	147×10^4
$K_p = \sqrt{\lambda R_p}$	8.03	9.07	9.95

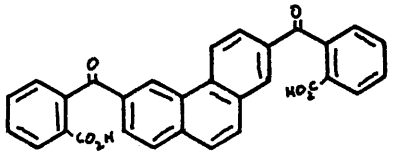
It will be of interest to extend the polyanthenes (28) (first member, anthracene) beyond the first two members to determine whether this series also follows the anellation principle.



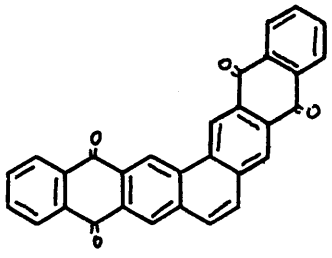
LI



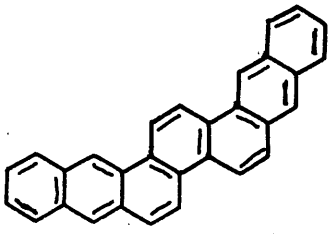
LII



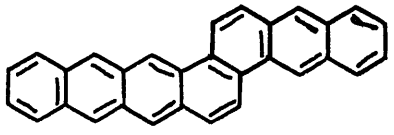
LIII



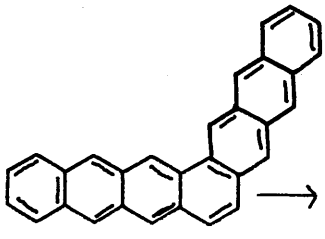
LIV



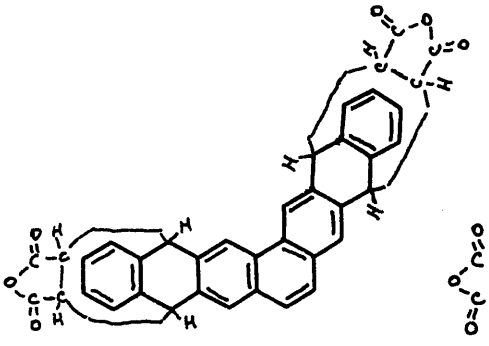
LV



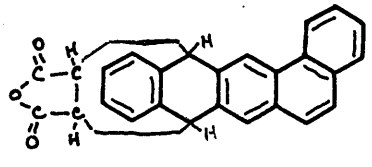
LVI



LVII



LVIII



LIX

The Syntheses of Heptaphene and 2:3-8:9-Dibenzopicene.

The position of substitution in polycyclic compounds in Friedel-Crafts reactions with acid chlorides or anhydrides is greatly influenced by the solvent used for the reaction. If the solvent can add to the acid chloride-or anhydride-aluminium chloride complex then the bulky complex is more likely to attack the sterically least hindered position or positions, in preference to other more reactive but more hindered positions (21). Thus phenanthrene yields 9-substituted products when benzene or methylene dichloride is used as solvent, but mainly 2 and 3-substituted products when nitrobenzene or carbon disulphide is used (35, 36).

Phenanthrene has been condensed with one molecule of phthalic anhydride in tetrachloroethane at 50-60° to give a mixture of 2-, 3-, and 9-o-carboxybenzoylphenanthrenes (37). In the present work, the products obtained by disubstitution of phenanthrene with phthalic anhydride were studied. Under the conditions used, substitution appeared to take place exclusively in the side rings of phenanthrene. The three hydrocarbons which were obtained by ring closure and reduction of the Friedel-Crafts reaction product are those one would expect from the four possible phenanthrenes, disubstituted in the 2, 3, 6 and 7 positions. These positions are equivalent to the β positions of naphthalene.

The phenanthrene was condensed with phthalic anhydride in the presence of aluminium chloride in tetrachloroethane at 95°. A uniform dicarboxylic acid crystallised from the tetrachloroethane solution after decomposition of the aluminium chloride complex and a mixture of dicarboxylic acids was obtained from the tetrachloroethane mother liquor. Assuming that substitution takes place in the sterically unrestricted 2, 3, 6 or 7 positions of the side rings, then the four possible di-o-carboxybenzoylphenanthrenes are the 3:6 (LI), 2:7 (LII), 3:7 (LIII) and the 2:6 isomers. In general a β substituent will cyclise to an α position, unless it is prevented by steric factors. Substituents on 2 and 7 will ring close to the positions 1 and 8 respectively, but substituents in the 3 and 6 positions will cyclise to the unhindered positions 2 and 7 respectively, rather than the hindered 4 and 5 positions. Therefore the most probable course of cyclisation of the acids (LI), (LII) and (LIII) are to the three ring systems of (LVII), (LV) and (LVI) respectively. The 2:6-acid would also form the structure (LVI).

The hydrocarbon heptaphene (LVII) was prepared from the uniform crystalline acid, therefore it is considered to be the 3:6-di-o-carboxybenzoylphenanthrene (LI). Ring closure of this acid with sulphuric acid at 160° gave a

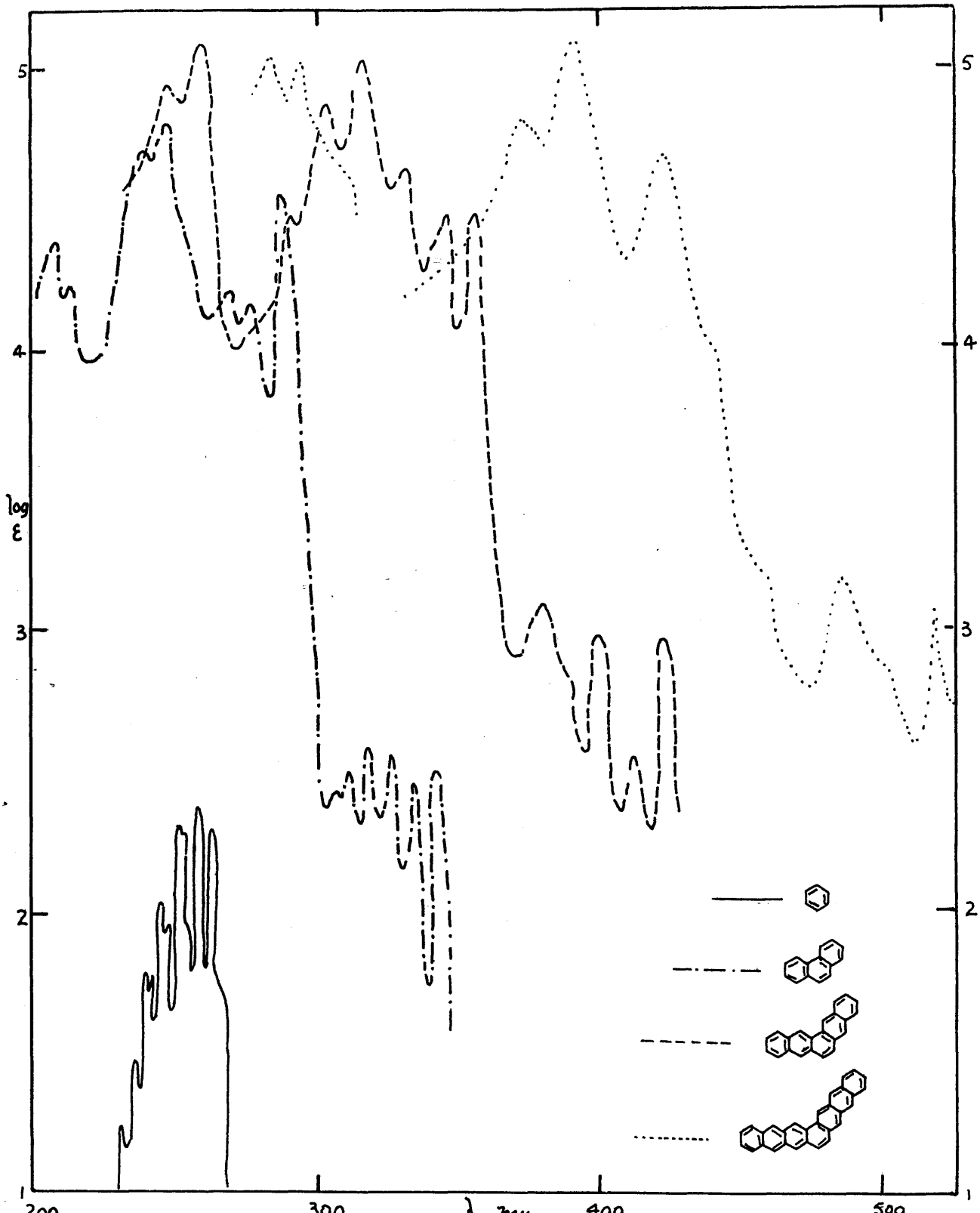
sparingly soluble diquinone (LIV). No other diquinone was observed from the cyclisation. The bright yellow diquinone was reduced by boiling pyridine, acetic acid and zinc dust (38) to an orange hydrocarbon. When the spectrum of this hydrocarbon is compared with those of benzene, phenanthrene (39) and pentaphene (40), (fig. 17), the similarity in type is immediately apparent. Heptaphene belongs to the "half-numbered" series of the phenes (see p. 6) and must have the order number K = $10\frac{1}{2}$. Therefore the first α and β bands can be calculated from the equations

$$\nu_\alpha = R_\alpha/K^2 \qquad \text{and} \qquad \nu_\beta = R_\beta/K^2$$

	α	β
K	10.5	10.5
R	2194600 $cm.^{-1}$	2962700 $cm.^{-1}$
1st band in gaseous state	19905	26873
Correction for solution in benzene	-350	-1200
Calculated 1st band in benzene	19555 $cm.^{-1}$ 511 mμ	25673 $cm.^{-1}$ 389mμ
Observed 1st band in benzene	516 mμ	385 mμ.

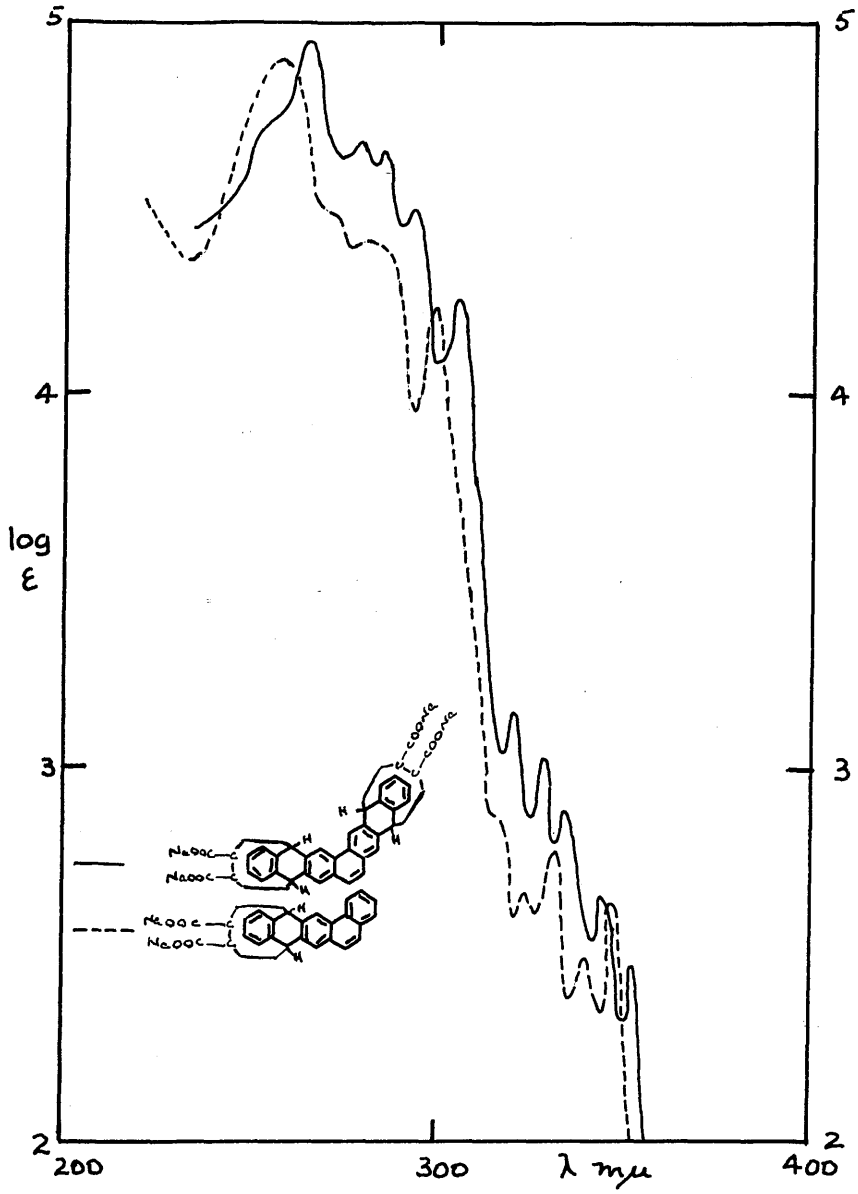
The p-bands do not follow the simple rules of the acene series.

Heptaphene reacted with two molecules of maleic anhydride to form the dianhydride (LVIII). The spectrum of (LVIII) is that of a phenanthrene derivative and its



Heptaphene (LVII). Maxima: 519, 503, 487, 457; 423, 391, 372 in 1:2:4-trichlorobenzene. 293.5, 283.5 in benzene. Pentaphene in alcohol. Phenanthrene in alcohol. Benzene in alcohol.

Fig. 17.



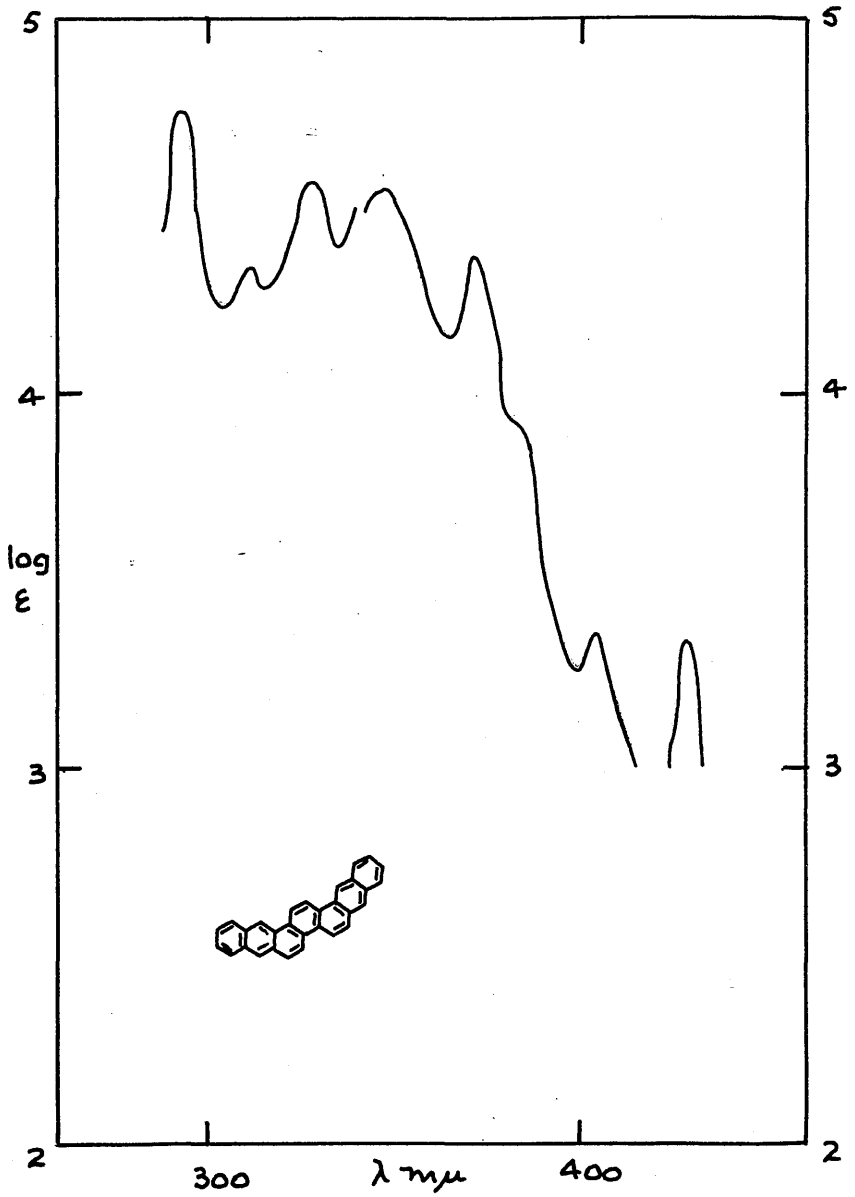
Tetrasodium salt from the maleic anhydride adduct (LVIII) in water. 352, 343, 334, 327.5, 319.5; 304, 293, 286, 279; 264.

Disodium salt from the maleic anhydride adduct of 1:2-benztetracene (LIX) in water. 348, 341, 333, 325; 299, 282; 257.

Fig. 18.

close similarity with that of the adduct of 1:2-benzotetracene (LIX) (41) is immediately obvious (Fig. 18).

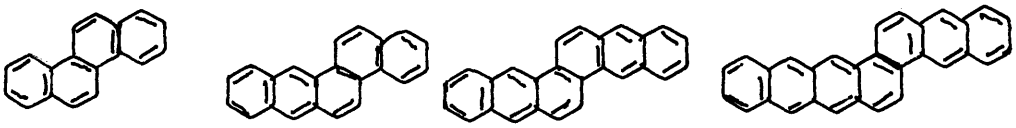
The mixture of isomeric acids from the tetrachloroethane mother liquor was cyclised with sulphuric acid, to give a mixture of quinones which was reduced with pyridine, zinc dust and acetic acid to give a mixture of hydrocarbons. No separation of the mixture was achieved by recrystallisation and the very low solubility of the hydrocarbons made complete chromatographic separation difficult, though a small quantity of a pale yellow hydrocarbon was isolated from the initial eluates from the chromatogram. This hydrocarbon was identical with a hydrocarbon obtained by treatment of the mixture in 1-methylnaphthalene solution with small portions of maleic anhydride until the first absorption bands of heptaphene (LVII) and a third hydrocarbon (bands at 487 and 457 mμ) had disappeared. The yellow hydrocarbon crystallised from the solution, free from its isomers. From the absorption spectrum of the hydrocarbon, (Fig. 19), it can be deduced that the hydrocarbon has not more than 3 linearly condensed rings. Also the fact that the hydrocarbon is the least reactive of the isomers, indicates that it has a less extended linear anellation than the other two. Therefore it is almost certainly 2:3-8:9-dibenzopicene (LV) and is derived from the acid (LII).



2:3-8:9-Dibenzopicene (LV). Maxima: 428, 404; 371, 345 in 1-methylnaphthalene; 326, 314; 293 in benzene.

Fig. 19.

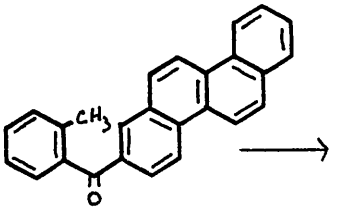
The third hydrocarbon was the most reactive of the three and therefore the most difficult to purify. It tended to oxidise on the column during chromatography. The hydrocarbon has approximately the first absorption band expected for the last member anthracenotetracene (LVI) of the anellation series chrysene, 3:4 benzotetraphene, anthracenoanthracene, (42).



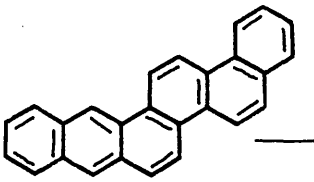
λ_{max} =	319	367	420	487
K_p =	7.429	7.929	8.482	9.13

The high reactivity of the hydrocarbon is also consistent with the structure of (LVI). Therefore the hydrocarbon is considered to be anthraceno(2':1'-1:2)tetracene. It is most probably formed by ring closure and reduction of the 2:6- and 3:7-di-o-carboxybenzoylphenanthrenes.

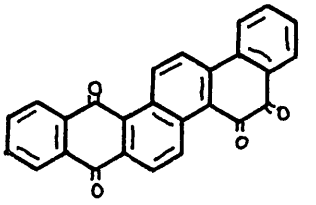
The fact that the absorption bands of the 3 hydrocarbons are in agreement with the predicted absorption bands of the 3 hydrocarbons expected from the Friedel-Crafts product, serves to confirm the structures assigned to them.



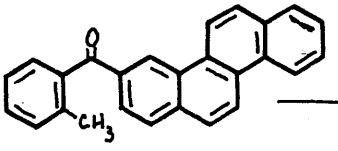
LX



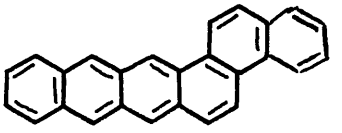
LXI



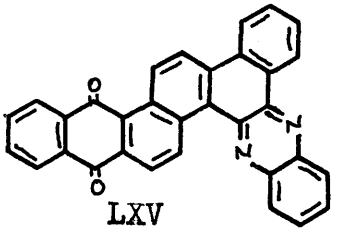
LXII



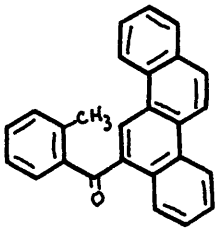
LXIII



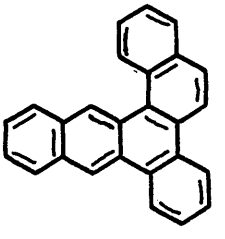
LXIV



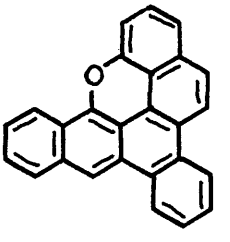
LXV



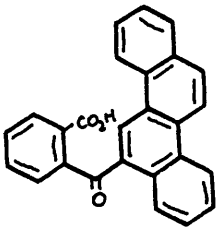
LXVI



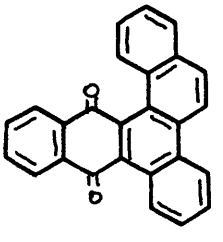
LXVII



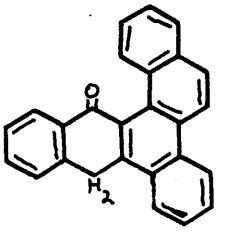
LXVIII



LXIX



LXX



LXXI

The Syntheses of Benzopicene and Naphthochrysene.

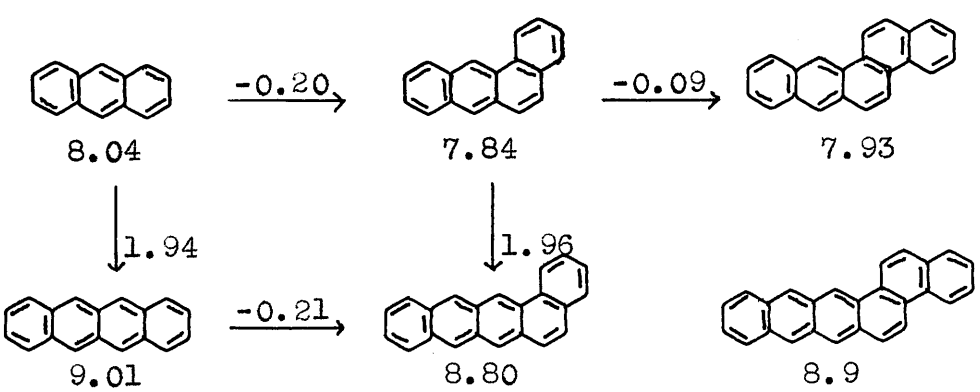
The behaviour of chrysene in Friedel-Crafts reactions is in many respects similar to that of phenanthrene. The most reactive position of chrysene is position 2 and substitution of acid chlorides or anhydrides occurs in this position in the presence of aluminium chloride when benzene or methylene dichloride is used as solvent (43, 44, 46), but 4- or 5-substituted (45) or a mixture of 2, 4 and 5 (46) substituted chrysenes are obtained when nitrobenzene or carbon disulphide is used.

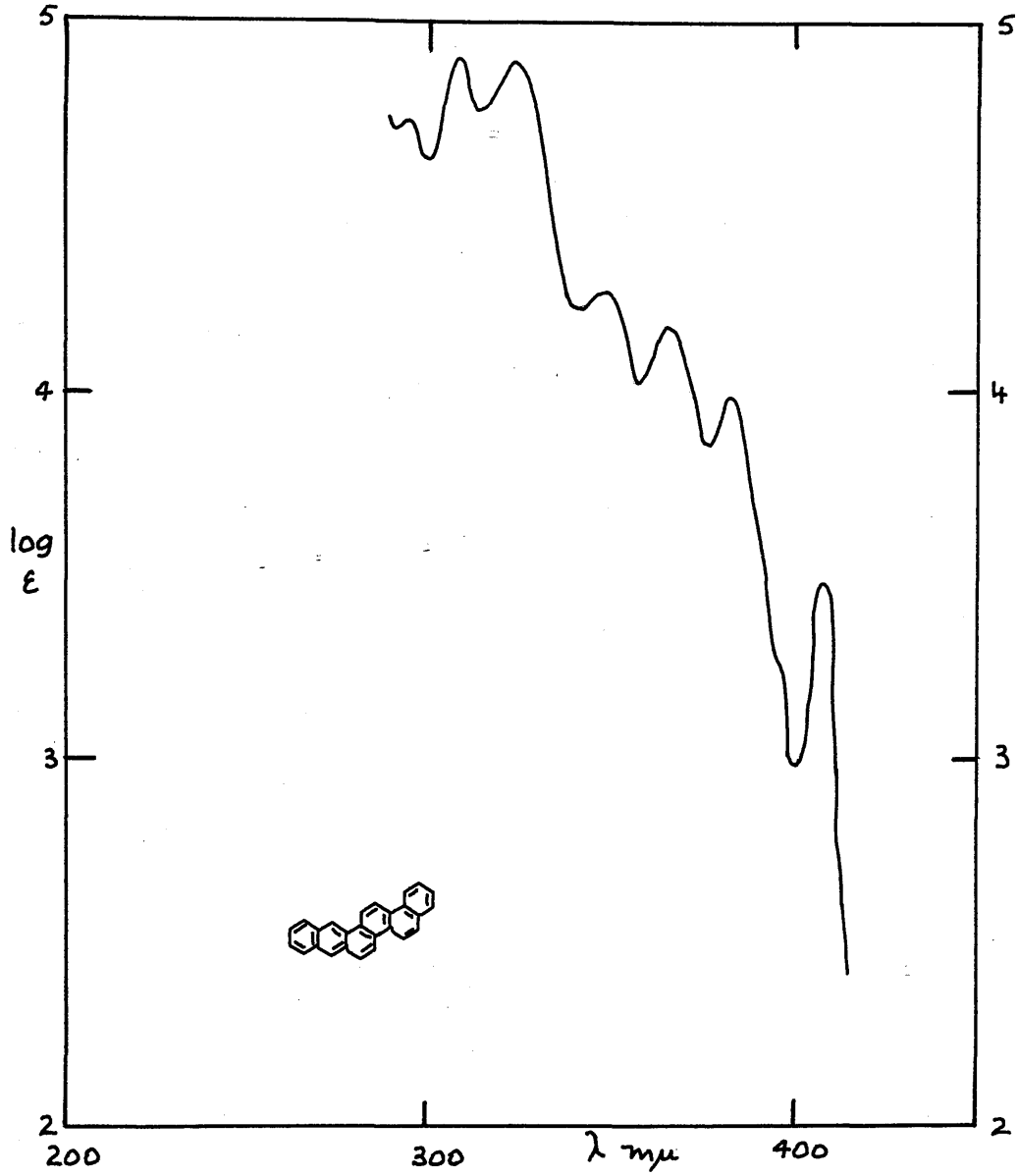
In the present work, the reactions of chrysene with o-toluoyl chloride and phthalic anhydride at 90°-100°, in the presence of aluminium chloride and tetrachloroethane as solvent, were studied. The ring systems obtained by cyclisation of the reaction products suggest that substitution occurred in positions 2, 4 and 5 of chrysene.

The condansation of chrysene with o-toluoyl chloride gave a mixture of ketones. No attempt was made to separate the mixture, but an Elbs cyclisation was carried out by pyrolysis of the ketones at 400°. The product obtained by sublimation of the pyrolysed material consisted of, apart from unchanged chrysene, two hydrocarbons and an oxygen-containing compound. The chrysene and the oxygen compound were separated by extraction with benzene. The

hydrocarbons were yellow (bands at 472 and 442 mμ) and a pale yellow (first band at 404 mμ). They could not be separated by crystallisation and, due to their slight solubility, only partial chromatographic separation was achieved. The yellow hydrocarbon was not obtained in a pure state. The pale yellow hydrocarbon was purified by crystallisation from a solution to which small portions of maleic anhydride were added until the bands at 472 and 442 mμ disappeared.

On the basis of its greater reactivity and position of its absorption bands, the yellow hydrocarbon most probably has the structure (XLIV) of a naphthotetracene. From a consideration of the following order number (K_p) relationships, naphthotetracene may be assumed to have an order number $K_p = 8.9$, which would require $\lambda = K_p^2/R =$ 462 mμ ($R = 1712800$ cm.$^{-1}$), compared to the observed value of 472 mμ.





2:3-Benzopicene (LXI) in benzene. Maxima: 405.5; 382, 363, 347; 324.5, 311, 298.

Fig. 20.

Naphthotetracene is the only system with four linearly condensed rings which would be formed in this synthesis.

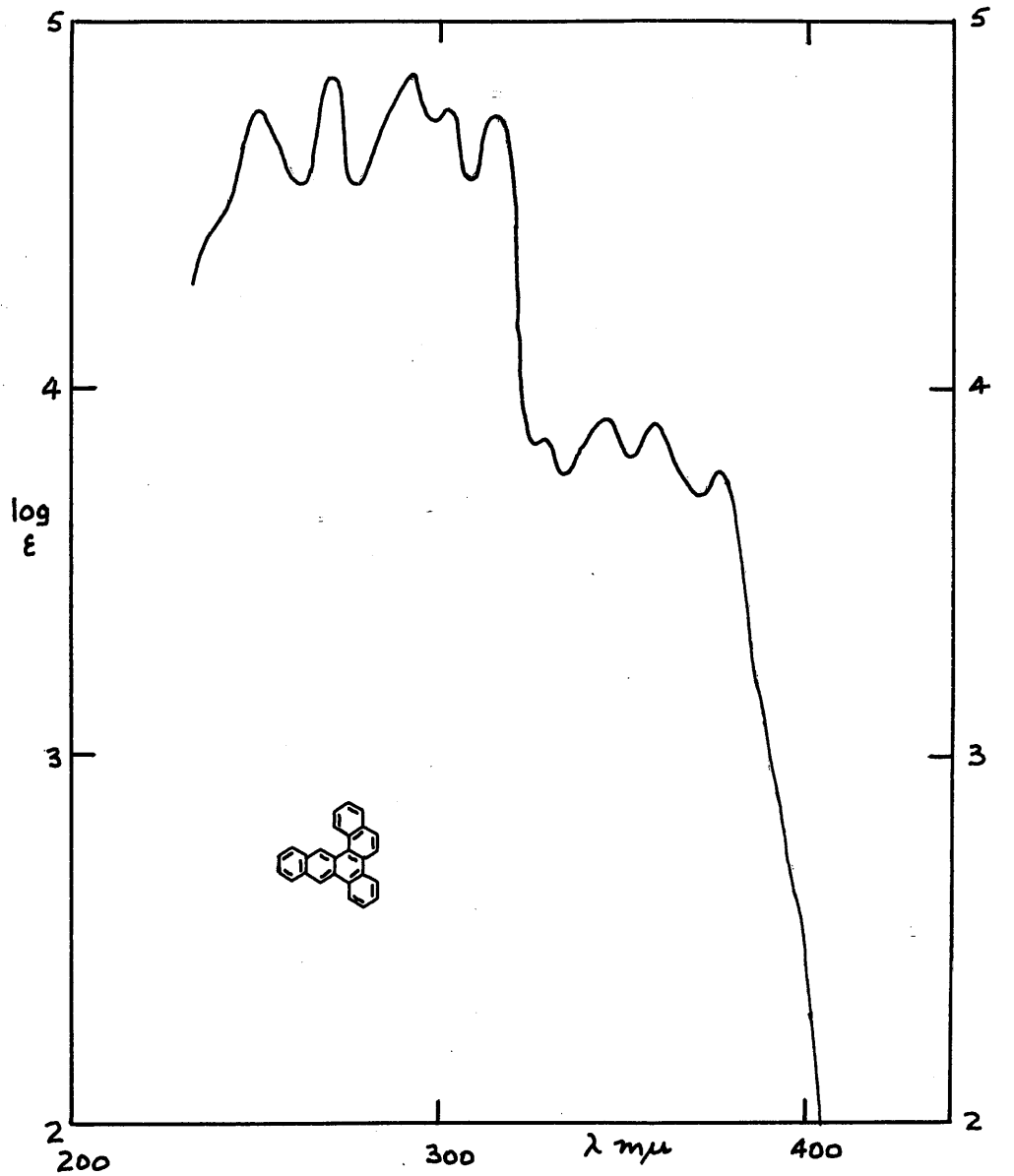
The less reactive pale yellow hydrocarbon is considered to be 2:3-benzopicene (LXI) the spectrum of which is given in Fig. 20. Oxidation of this hydrocarbon with chromic anhydride in acetic acid gave a diquinone. This must contain an o-quinone group since it gave a phenazine derivative with o-phenylenediamine. There are two possible diquinones, the 1:4-5:6- and the 1:4-11:12-diquinone. The former would yield an azine (cf. Clar (46a)), but no reaction occurred with hydrazine hydrate, therefore the diquinone and the phenazine must have the structures (LXII) and (LXV) respectively.

The two hydrocarbons are most probably derived from the 4- and 5-o-toluoylchrysenes respectively, the course of ring closure being influenced by the same factors as applied to the cyclisation of the di-o-carboxybenzoylphenanthrenes (see p. 36).

The oxygen containing compound from the pyrolysed product was found to be identical with a compound derived from 2-o-carboxybenzoylchrysene (44), therefore substitution must also have occurred in the 2 position of chrysene.

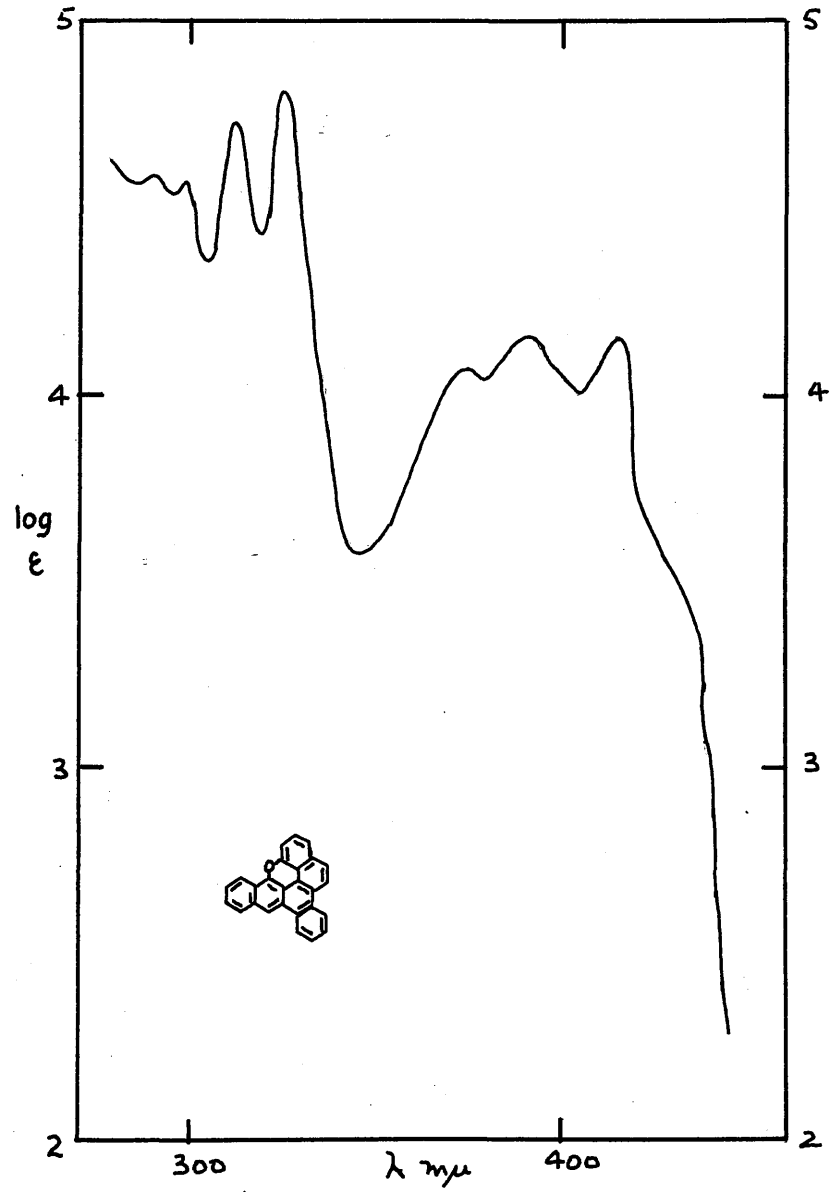
When chrysene was treated with phthalic anhydride under

similar conditions to those used for o-toluoyl chloride, a mixture of acids was obtained, though the 2-o-carboxybenzoylchrysene (LXIX) (44) could be isolated through its ammonium salt. This acid was cyclised to the quinone (LXX) with benzoyl chloride (47). Reduction of (LXX) with pyridine, zinc dust and acetic acid gave the hydrocarbon naphtho(2':3'-1:2)chrysene (LXVII), the spectrum of which is given in Fig. 21. A yellow by-product of the reduction was identical with the oxygen-containing compound from the Elbs pyrolysis. It was also identical with the compound obtained by Beyer and Richter (44) from the reduction of the quinone (LXX) in a zinc dust melt. Beyer and Richter considered the compound to be the anthrone (LXXI), but reported that it did not have any of the properties expected of a compound with such a structure. It did not enolise with alkali, form an acetyl derivative, react with any of the usual ketonic reagents, and could not be reduced further. Since the compound has almost certainly the cyclic epoxy structure (LXVIII), the lack of reactivity of the oxygen is to be expected. The analysis obtained are consistent with the formula of (LXVIII), although it contains two hydrogen atoms less than Beyer and Richter's anthrone formulation. The spectrum of (LXVIII) is given



Naphtho(2':3'-1:2)-chrysene (LXVII) in alcohol.
Maxima: 376, 361, 346, 328; 315, 302; 292, 270, 249.

Fig. 21.



12:1'-Oxido-naphtho(2':3'-1:2)-chrysene (LXVIII) in benzene. Maxima: 414, 391, 372; 326, 311.5, 298, 289.

Fig. 22.

in Fig. 22. The red shift when compared with the spectrum of (LXVII) is similar to that shown in Fig. 10 between benzoperylene (XXXV) and oxido-benzoperylene (XXXIX).

When the mixture of acids from the mother-liquor, after the separation of the acid (LXIX), was cyclised and the mixture of quinones reduced as above, a mixture of the two hydrocarbons (LXI) and (LXIV) was obtained. Therefore substitution in the side ring must also have occurred in the reaction of phthalic anhydride with chrysene.

EXPERIMENTAL.

Melting points are uncorrected and were taken in evacuated capillaries. Microanalyses are by Mr. J.M.L. Cameron, Miss M.W. Christie and Miss R.H. Kennaway. Absorption spectra were mostly recorded on a Unicam SP500 spectrometer.

Syntheses of Diperinaphthyleneanthracenes.

1:5-Dichloro-9:10-dihydro-9:10-di-1'-naphthylanthracene-9:10-diol (VII). - A suspension of finely powdered 1:5-dichloroanthraquinone (35 g.) in benzene (350 ml.) was added with stirring during 15 min. to 1-naphthylmagnesium bromide prepared from 1-bromonaphthalene (103 g.) and magnesium (12 g.) in ether (200 ml.). The temperature was allowed to rise during the addition. 200 ml. of solvent were distilled from the mixture, which was then heated under reflux on a water-bath for 2 hr. with continuous stirring. The thick suspension was decomposed by pouring it into dilute acetic acid containing ice. Benzene and some naphthalene were removed by steam distillation. The product was triturated and

washed with ether (400 ml.), digested thoroughly with a large excess of alkaline sodium dithionite solution to remove unchanged starting material, and washed with hot water, a pale fawn solid (38 g.) being obtained. Crystallisation from 1:2:4-trichlorobenzene gave colourless prisms m.p. 328-329° (decomp.), of the diol (VII) (Found: C, 76.5; H, 4.5; Cl, 13.5. $C_{34}H_{22}O_2Cl_2$ requires C, 76.6; H, 4.2; Cl, 13.3%). The compound gave a transient green colour changing to brown, in concentrated sulphuric acid.

1:5-Dichloro-9:10-di-1'-naphthylanthracene (VIII). - A suspension of the diol (VII) (25 g.) in acetic acid (150 ml.) and hydriodic acid (21 ml. 55%) was heated under reflux for 15 min., cooled, filtered, and washed with acetic acid and benzene, to give a yellow product (21 g.) which crystallised from 1:2:4-trichlorobenzene, yellow prisms, m.p. 338-339°, of 1:5-dichloro-9:10-di-1'-naphthylanthracene (VIII) being obtained (Found: C, 81.9; H, 4.0; Cl, 14.0. $C_{34}H_{20}Cl_2$ requires C, 81.8; H, 4.0; Cl, 14.2%). The sample for analysis was sublimed under vacuum. The compound was insoluble in concentrated sulphuric acid.

1:9-5:10-Diperinaphthyleneanthracene (IX). - A mixture of 1:5-dichloro-9:10-di-1'-naphthylanthracene (2 g.), powdered potassium hydroxide (10 g.) and quinoline (12 ml.) was heated under reflux for 45 min. The colour of the solution changed through deep red, violet-red, and bluish-violet to blue. The quinoline layer was decanted into dilute hydrochloric acid and the deep-blue precipitate, after being filtered off and washed with hydrochloric acid and water, was sublimed in vacuum at 300-310°/8 x 10^{-5} mm. Crystallisation of the sublimate (1 g.) from xylene gave deep blue prisms with a coppery sheen, m.p. 333-334°, of 1:9-5:10-diperinaphthylene-anthracene (IX) (Found: C, 95.8; H, 4.2. $C_{34}H_{18}$ requires C, 95.75; H, 4.25%). When mixed with a sample of the hydrocarbon obtained by Clar and Guzzi (6), it melted at 288-296°. In concentrated sulphuric acid it gave a green colour which quickly became pinkish brown. Its solution in xylene was blue with a red fluorescence.

Maleic Anhydride Adduct (VI). - The hydrocarbon (IX) (40 mg.) and maleic anhydride (30 mg.) were heated under reflux in xylene (20 ml.) for 5 min.

The solution became a faint bluish colour but did not become colourless. During the reaction, the adduct crystallised as colourless prisms with a faint bluish tinge (Found: C, 87.0; H, 4.0. $C_{38}H_{20}O_3$ requires C, 87.0; H, 3.8%). Above 200°, the adduct gradually decomposed to give the blue hydrocarbon.

1:4-Dichloro-9:10-dihydro-9:10-di-1'-naphthyl-anthracene-9:10-diol (IV). - The diol was prepared by Wright (7) in a similar manner to (VII), but starting from 1:4-dichloroanthraquinone, crystallisation from xylene and nitrobenzene gave colourless prisms, m.p. 312-313° (decomp.), which dissolved in concentrated sulphuric acid to a dark greenish-brown solution.

1:4-Dichloro-9:10-di-1'-naphthylanthracene (V). - The diol (IV) was reduced as described above for the corresponding 1:5-dichloro-compound. The product crystallised from xylene, pale yellow needles, m.p. 341-342°, of 1:4-dichloro-9:10-di-1'-naphthylanthracene (V) being obtained (Found: C, 81.5; H, 4.5; Cl, 13.9. $C_{34}H_{20}Cl_2$ requires C, 81.8; H, 4.0; Cl, 14.2%). It was insoluble in concentrated sulphuric acid.

1:9-4:10-Diperinaphthyleneanthracene (II). - A mixture of the 1:4-dichloro-compound (V) (0.5 g.), potassium hydroxide (2.5 g.) and quinoline (3 ml.) was heated under reflux. A much shorter time sufficed to effect ring closure than with the corresponding 1:5 compound. The quinoline solution became blue within 5 minutes. Heating was continued for a further 15 minutes and the quinoline solution treated as above. The blue precipitate yielded 0.35 g. sublimate which crystallised from 1:2:4-trichlorobenzene as dark green-blue prisms or needles, m.p. 348-350^{0} of the hydrocarbon (II). (Found: C, 95.9; H, 4.3. Calc. for $C_{34}H_{18}$: C, 95.75; H, 4.25%). There was no depression of the melting point when mixed with the hydrocarbon of Clar and Guzzi (6) or that of Wright (7).

The Syntheses of Circumanthracene and Dinaphtho(7':1'-1:13)(1":7"-6:8)peropyrene.

Dinaphtho(7':1'-1:13)(1":7"-6:8)peropyrene-2:3:9:10-tetracarboxylic Dianhydride (XIII). - Diperinaphthyleneanthracene (IX) (2 g.) and maleic anhydride (25 g.) were heated under reflux for 15 min. The initial

addition product, the colourless adduct (VI) was deposited from solution. Chloranil (7 g.) was added and the adduct gradually redissolved. The reaction continued for 2¼ hr. during which time the colour changed from violet-red to reddish brown, and a solid precipitated. Boiling xylene was added and the precipitate filtered off hot and washed with hot xylene. The dark purplish precipitate of the dianhydride (XIII) could not be successfully crystallised from any solvent. It was dissolved in ethanolic potassium hydroxide, and the solution diluted with water and acidified to give a dark purplish-red precipitate of the tetracarboxylic acid (Found: C, 76.4; H, 3.1. $C_{42}H_{18}O_8$ requires C, 77.5; H, 2.8%). The acid dissolved in warm concentrated sulphuric acid to a greenish-blue solution.

Dinaphtho(7':1'-1:13)(1":7"-6:8)peropyrene (XIV) and Circumanthracene (XV). - (a) Decarboxylation with soda-lime. The dianhydride (2.4 g.) and soda-lime (20 g.) were ground together to a smooth paste with a little alcohol. The mixture was heated at about 400°/1 mm. until no further material sublimed

(about 12 hr.). The sublimate was extracted several times with boiling xylene. The crystals which separated from the combined extracts were filtered off and the xylene filtrate was concentrated and chromatographed on alumina with benzene as eluant. The orange-red eluate had a green fluorescence and yielded fine orange-red needles (0.1 g.) m.p. 338-339°, of dinaphthoperopyrene (XIV) (Found: C, 96.3; H, 3.8. $C_{38}H_{18}$ requires C, 96.2; H, 3.8%). It dissolved in warm concentrated sulphuric acid to a magenta solution.

The residue from the xylene extraction was crystallised from 1:2:4-trichlorobenzene, and the crystals were combined with those from the xylene extraction and chromatographed on alumina with trichlorobenzene as eluant. The first, reddish-band yielded a small quantity of dinaphthoperopyrene. A second, reddish-purple band on elution gave a deep-red solution from which were obtained long black-looking needles of circumanthracene (XV) which sinter at 480° but do not melt clearly at higher temperatures (Found: C, 96.3, 96.5; H, 3.45, 3.6. $C_{40}H_{16}$ requires C, 96.75; H, 3.25%). It dissolved with an orange-colour in concentrated sulphuric acid.

(b) Decarboxylation with copper powder. A small quantity of the dianhydride (XIII) was heated with some copper powder in quinoline for 2 hr. The quinoline solution was filtered into dilute hydrochloric acid and the precipitate sublimed in a vacuum. The dark reddish sublimate contained no trace of circumanthracene and on purification was identical with the dinaphthoperopyrene obtained as above.

The Synthesis of 3:4-5:6-10:11-12:13-Tetrabenzoperopyrene.

1:5-Dichloro-9:10-dihydro-9:10-di-(2'-methyl-1'-naphthyl)anthracene-9:10-diol (XXI). - A suspension of finely powdered 1:5-dichloroanthraquinone (35 g.) in benzene (300 ml.) was added with stirring during 30 min. to 2-methyl-1-naphthylmagnesium bromide prepared from 1-bromo-2-methylnaphthalene (110 g.) and magnesium (12 g.) in ether (250 ml.). The temperature was allowed to rise during the addition. 250 ml. of solvent were distilled from the mixture which was then heated under reflux on a water bath for 2 hr. with continuous stirring. The thick suspension was decomposed by pouring it into dilute acetic acid containing ice. Benzene and some

methylnaphthalene were removed by steam-distillation. The product was triturated with ether (1 l.) and digested twice with a large excess of alkaline sodium dithionite solution, a light fawn powder (26 g.) being obtained. Crystallisation from 1:2:4-trichlorobenzene gave the colourless diol (XXI), m.p. 329-330° (decomp.) (Found: C, 77.1; H, 4.8; Cl, 13.1. $C_{36}H_{26}O_2Cl_2$ requires C, 77.0; H, 4.7; Cl, 12.6%). It dissolved to give a green colour in concentrated sulphuric acid.

1:5-Dichloro-9:10-di-(2'-methyl-1'-naphthyl)anthracene (XXII). - A suspension of the diol (XXI) (10 g.) in acetic acid (70 ml.) and 55% hydriodic acid (7 ml.) was heated under reflux for 1 hr. The product was sublimed in a vacuum and the yellow sublimate (7 g.) was crystallised from 1:2:4-trichlorobenzene to give pale yellow 1:5-dichloro-9:10-di-(2'-methyl-1'-naphthyl) anthracene (XXII), m.p. 359-360° (Found: C, 82.25; H, 5.1; Cl, 13.0. $C_{36}H_{24}Cl_2$ requires C, 82.0; H, 4.6; Cl, 13.4%). It was insoluble in concentrated sulphuric acid.

7':7"-Dimethyl-1:9-5:10-diperinaphthyleneanthracene (XXIII). - A mixture of the reduced 1:5-dichloro

compound (2 g.), potassion hydroxide (5 g.), and quinoline (11 ml.) was heated under reflux for 23 min. in an atmosphere of nitrogen. The reddish-violet solution was poured into dilute hydrochloric acid and the dark blue precipitate was extracted with benzene (150 ml.). The extract was chromatographed on alumina, the column being protected from the light. Elution, under pressure, with benzene-light petroleum (b.p. 40-60°) (1:2) gave an orange solution with a green fluorescence of the monocyclised compound, the benzoperylene derivative. A second blue band was eluted with benzene and yielded deep blue crystals, m.p. 382-383°, of the hydrocarbon (XXIII) (Found: C, 94.95; H, 4.8. $C_{36}H_{22}$ requires C, 95.1; H, 4.9%). The blue solution, which has a red fluorescence, was photooxidised quickly. The compound dissolved in concentrated sulphuric acid to give a reddish-brown solution.

3:4-5:6-10:11-12:13-Tetrabenzoperopyrene (XXVI). - A mixture of the reduced dichloro-compound (5 g.), potassium hydroxide (25 g.), and quinoline (30 ml.) was heated under reflux for 90 min. The quinoline solution was poured into dilute hydrochloric acid, and the dark precipitate was extracted (Soxhlet)

with xylene until the extract was almost colourless. The red xylene solution yielded a small quantity of a very soluble, red mixture of compounds which were not identified. The residue from the xylene extraction was then extracted with 1:2:4-trichlorobenzene to give a low yield of orange-brown leaflets. They were dissolved in trichlorobenzene and chromatographed on alumina at 140° with trichlorobenzene as eluant. The yellow eluate had a strong green fluorescence and yielded orange feathery needles, m.p. 487-488°, of tetrabenzoperopyrene (Found: C, 96.3, H, 3.9. $C_{36}H_{16}$ requires C, 96.4; H, 3.6%). The compound dissolved in hot concentrated sulphuric acid to give a green solution.

The Synthesis of 1:2-Benzoperylene.

1:5-Di-2'-naphthyloxyanthraquinone (XXXI). - This was prepared as described by Stewart (23) who modified a method of Scholl, Bottger and Wanka (48). An intimate mixture of 1:5-dichloroanthraquinone (37 g.), β-naphthol (75 g.) and powdered potassium hydroxide (22 g.) was heated at 145° for 2 hr. The melt, mobile at first, became very viscous. The cold melt was extracted with boiling,

dilute, aqueous potassium hydroxide and crystallised from nitrobenzene to give large yellow prisms (65 g.), m.p. 245-247°. The compound dissolved in concentrated sulphuric acid to a violet-blue solution and gave a yellow vat in alkaline sodium dithionite solution.

4:2'-12:1"-Dioxido-3:1'-naphthyl-1:2-benzperylene (XXXIII) and 4:2'-8:2"-dioxido-1:9-5:10-diperinaphthyleneanthracene (XXXVI). - A mixture of the dinaphthyloxyanthraquinone (XXXI) (26 g.), sodium chloride (26 g.), and aluminium chloride (140 g.) was heated at 175-180° for 35 min. After cooling to 110°, the melt was poured into dilute hydrochloric acid. The blue-black precipitate was extracted with warm alkaline sodium dithionite solution, dried, and extracted in a Sohxlet apparatus with xylene. There was no trace of the red compound (XXXII). The extraction was continued until the xylene was a faint blue colour. The xylene solution was concentrated to give blue crystals (2.5 g.), m.p. >400°, of the dioxide (XXXIII) (Found: C, 88.9; H, 3.6. $C_{34}H_{16}O_2$ requires C, 89.5; H, 3.5%). It sublimed in a vacuum without decomposition and

dissolved in concentrated sulphuric acid to a violet solution with a red fluorescence. The residue from the xylene extraction was sublimed in a vacuum at $400^{\circ}/8 \times 10^{-5}$ mm. The blue green sublimate was extracted with boiling xylene and crystallised from 1:2:4-trichlorobenzene, It was resublimed and recrystallised several times, to give dark greenish-blue needles, m.p. 515-516°, of the dioxide (XXXVI) (Found: C, 90.0; H, 3.8. $C_{34}H_{14}O_2$ requires C, 89.85; H, 3.1%). It dissolves in concentrated sulphuric acid to a blue solution with a very strong red fluorescence.

9:10-Di-1-naphthylanthracene (XXXIV). - Naphthyl lithium was prepared according to the method of Gilman, Zoellner and Selby (49), except that the lithium was prepared in a finely divided form by the method of Woodward et al. (50), by melting the lithium under liquid paraffin and shaking it into small particles. Reaction of the naphthyl lithium and anthraquinone gave 9:10-dinaphthyl-9:10-dihydroanthracene-9:10-diol (XXXVII) in 78% yield. The diol was reduced to 9:10-di-1'-naphthylanthracene by heating under reflux with acetic acid and potassium iodide.

1:2-Benzoperylene (XXXV). - The dinaphthylanthracene (44 g.) was added to sodium chloride (45 g.) and aluminium chloride (230 g.) at 125°, heated to 160° during 5 min., cooled, and poured into dilute hydrochloric acid. The blue-black precipitate was dried and extracted with 400 ml. of cold benzene. The extract was taken to dryness and the residue was distilled in a high vacuum giving a first colourless fraction (mainly anthracene) and a second, red, resinous fraction (4 g.). The residue in the flask was mainly 1:9-4:10-diperinaphthylene-anthracene. The second fraction was redistilled into two fractions, the first of which was washed with a little benzene and crystallised from benzene, to give yellow plates, m.p. 268-270°, of perylene. The second was very slowly fractionally sublimed; the yellow portion which sublimed first was perylene; the red fraction which sublimed as droplets was dissolved in benzene and chromatographed; the benzene eluate of the orange band was taken to dryness and the residue crystallised from light petroleum (b.p. 60-80°) to give red needles, m.p. 115-116°, of 1:2-benzoperylene (XXXV) (Found: C, 94.9; H, 4.8%; M (Rast), 310. $C_{24}H_{14}$ requires C, 95.3; H, 4.7%;

M, 302). It dissolved in concentrated sulphuric acid to a green solution with a red fluorescence. Its solution in organic solvents had a green fluorescence, and photo-oxidised rather quickly.

Adduct of 1:2-Benzoperylene and Maleic Anhydride (XXXVIII). - 1:2-Benzoperylene (XXXV) was heated under reflux in benzene with a large excess of maleic anhydride until the solution became colourless. The adduct recrystallised from acetic anhydride as colourless prisms, m.p. 300-306° (decomp.) (Found: C, 83.6; H, 4.4. $C_{28}H_{16}O_3$ requires C, 84.0; H, 4.0%). It dissolved in hot concentrated sulphuric acid to a green solution with a red fluorescence.

1-Chloro-9:10-dihydro-9:10-di-1'-naphthylanthracene-9:10-diol (XLII). - A suspension of finely powdered 1-chloroanthraquinone (12.1 g.) in benzene (100 ml.) was slowly added with stirring to 1-naphthylmagnesium bromide prepared from 1-bromonaphthalene (41.4 g.) and magnesium (4.8 g.) in ether (70 ml.). The temperature was allowed to rise during the addition. 70 ml. of Solvent were distilled from the mixture which was then heated under reflux for 2 hr, with stirring. The suspension was poured into dilute

acetic acid. The residue remaining after steam-distillation was washed with ether and digested thoroughly with alkaline sodium dithionite solution, an almost colourless powder (12.3 g.) being obtained. Crystallisation from xylene gave colourless prisms, m.p. 291-292° (decomp.) of the diol (XLII) (Found: C, 81.6; H, 4.8; Cl, 6.9. $C_{34}H_{23}O_2Cl$ requires C, 81.8; H, 4.65; Cl, 7.1%). In concentrated sulphuric acid it dissolved to a green solution.

1-Chloro-9:10-di-1'-naphthylanthracene (XLI). - A suspension of the diol (XLII) (5 g.) in acetic acid (30 ml.) and hydriodic acid (55%, 4.5 ml.) was heated under reflux for 15 min. A pale yellowish powder (3.9 g.) was obtained which crystallised from xylene as yellow prisms, m.p. 297-298°, of 1-chloro-9:10-di-1'-naphthylanthracene (Found: C, 88.1; H, 4.45; Cl, 7.4. $C_{34}H_{21}Cl$ requires C, 87.8; H, 4.55; Cl, 7.6%). It was insoluble in concentrated sulphuric acid.

3-1'-Naphthyl-1:2-benzoperylene (XL). - 1-Chloro-9:10-di-1'-naphthylanthracene (2 g.) in quinoline (15 ml.) was heated under reflux with potassium hydroxide (10 g.) for 7 min. The quinoline solution,

which had quickly become red with a green fluorescence, was decanted into dilute hydrochloric acid. The orange-red precipitate was sublimed in a vacuum. The sublimate was dissolved in benzene and the solution chromatographed on alumina. An orange-red band was eluted with benzene-light petroleum (b.p. 40-60°; 3:1). Crystallisation from light petroleum (b.p. 80-100°), by adding the petroleum to the benzene concentrate and distilling off the benzene, gave red prisms, m.p. 198-200°, of 3-1'-naphthyl-1:2-benzoperylene (XL) (Found: C, 95.3; H, 4.8%; M (Rast) 436. $C_{34}H_{20}$ requires C, 95.3; H, 4.7% M, 428). The solution of the compound was orange with a green fluorescence and it photo-oxidised rapidly. The hydrocarbon dissolved in concentrated sulphuric acid to give a green solution with a red fluorescence.

The Synthesis of Terrylene and Quaterrylene.

7:8-Dichloroterrylene (XLV). - This compound was prepared in collaboration with Mr. R.M. Laird, who also prepared the 2:3-dichloro-1:4-di-1'-naphthyl-

naphthalene (XLIV) by reduction of the diol (XLIII) obtained from the Grignard reaction of 2:3-dichloronaphthoquinone and 1-bromonaphthalene.

2:3-Dichloro-1:4-di-1'-naphthylnaphthalene was added to a melt of sodium chloride (15 g.) and aluminium chloride (75 g.) at 110°. The melt was kept at 115° for 5 min. and then poured into dilute hydrochloric acid. The precipitate was thoroughly washed with hot water, dried and extracted with benzene. The benzene extract was chromatographed on alumina, and eluted with benzene. A first yellow band gave yellow plates, m.p. 272-274°. In concentrated sulphuric acid they dissolved to give a transient green colour which changed to violet. When mixed with an authentic specimen of perylene the compound melted at 272-274°.

The compound obtained from a second orange-red band gave, on recrystallisation from xylene, small orange plates, m.p. 434-436°. It dissolved in concentrated sulphuric acid to give a violet solution. It was spectroscopically identical with the compound, hitherto called terrylene, obtained by Clar (28). When a sample of this compound was chromatographically purified, its melting point

and mixed melting point were identical with that of the above compound. A. Zinke et al. (32) give a melting point of 440-442° for their "hydrocarbon 2". The structure of this compound is still unknown.

A third, violet-red band gave, on elution, dark violet-red needles of 7:8-dichloroterrylene (XLV) which, after being recrystallised from xylene, melted at 308-310° (Found: C, 80.7; H, 3.4; Cl, 16.2. $C_{30}H_{14}Cl_2$ requires C, 80.9; H, 3.2; Cl, 15.9%). The compound dissolved in concentrated sulphuric acid to give a blue solution. Its violet-red solution in organic solvents shows a strong yellow fluorescence.

The above chromatographic separation can be carried out more quickly if the reaction product is extracted with cold benzene to remove perylene and the residue dissolved in hot xylene and chromatographed at 120°, using xylene as eluant.

Octahydroterrylene (XLVIII). - A mixture of dichloroterrylene (190 mg.), red phosphorus (50 mg.) and 55% hydriodic acid (3.5 ml.) was heated in a sealed tube at 210° for ten hours. The dark product (170 mg.) was dried, powdered and extracted with benzene (160 ml.). A residue of 38 mg. remained.

The benzene solution was chromatographed on alumina. A first small colourless, violet fluorescent band was quickly followed by a yellow band which yielded a pale yellow crystalline powder (82 mg.), m.p. 390-393° of 4:5:6:7:8:9:10:11-octahydroterrylene (XLVIII) (Found: C, 93.7; H, 6.1. $C_{30}H_{24}$ requires C, 93.7; H, 6.3%). It dissolves in hot concentrated sulphuric acid to give a yellow-green solution which changes to blue. The absorption spectrum of the compound indicates the presence of a small quantity (some 2%) of a less highly hydrogenated terrylene. The bands at 474 and 426 mμ suggests that it may be a derivative of dibenzopyrene (XLVII).

A last violet-orange band of the chromatogram was eluted with benzene and some alcohol and yielded violet plates (5 mg.) of terrylene (see below).

Dichloroterrylene (0.2 g.) can also be reduced by heating it under reflux with a mixture of red phosphorus (1 g.), hydriodic acid (20 ml.) and xylene (50 ml.) for 6 days. The reaction product yielded an octahydroterrylene identical with that above. It also contained the compound with bands at 474 and 426 mμ.

Terrylene (XLVI). - Octahydroterrylene (40 mg.) was sublimed under vacuum in a current of carbon dioxide through 20% palladium-charcoal (granular) at 380°. The purple red sublimate gave, on recrystallisation from 1:2:4-trichlorobenzene, red violet plates (23 mg.), m.p. 510-511° of terrylene (XLVI) (Found: C, 95.7; H, 4.2. $C_{30}H_{16}$ requires C, 95.7; H, 4.3%). It dissolved in concentrated sulphuric acid to give a blue solution with a red fluorescence. The rose coloured solution in organic solvents showed an orange fluorescence.

The residue (38 mg.) remaining after the benzene extraction of the above hydriodic acid reduction product consisted mostly of terrylene, which, by sublimation and crystallisation from 1:2:4-trichlorobenzene could be obtained pure.

Quaterrylene (XLIX). - Finely powdered perylene (2 g.) was added to a melt of sodium chloride (4 g.) and aluminium chloride (20 g.) and kept at 150° for 20 min. with stirring. The melt was poured into dilute hydrochloric acid, boiled and washed thoroughly with water and dilute ammonia. The dried residue was sublimed under vacuum in a stream of carbon dioxide at 0.01 mm. At 240° unreacted perylene

(0.6 g.) sublimed. At 400° a reddish-brown compound was obtained. Chromatography at 140°, on alumina gave, first, a little perylene and then, from a brownish-red band, red-brown feathery needles (80 mg.), m.p. 467-469° of a hydrocarbon (Found: C, 96.0; H, 4.3%). The compound dissolved in hot concentrated sulphuric acid to give a blue solution.

The sublimation was continued at a considerably higher temperature and a sublimate (0.3 g.) with a deep green sheen was obtained. Traces of the reddish-brown hydrocarbon were removed by boiling the powdered substance repeatedly with a liquid trimethylnaphthalene mixture in which it is quite insoluble in the cold. The compound crystallised from molten pyrene, (m.p. 156°), the melting point of which has been lowered by the addition of some phenanthrene. From the blue solution were obtained large plates with a green sheen, m.p. >570° of quaterrylene (XLIX) (Found: C, 95.8, 95.8; H, 4.1, 4.1. $C_{40}H_{20}$ requires C, 96.0; H, 4.0%). It dissolved in concentrated sulphuric acid to give a greenish blue solution. The powdered substance was blue.

The Syntheses of Heptaphene and 2:3-8:9-Dibenzopicene.

3:6-Di-o-carboxybenzoylphenanthrene (LI) and Isomeric Acids (LII) and (LIII). - Finely powdered phenanthrene (90 g.) was added to a mixture of phthalic anhydride (222 g.) and powdered aluminium chloride (400 g.) in tetrachloroethane (330 ml.) at 95°. This temperature was maintained with frequent shaking, for 75 minutes. After decomposition of the reaction mixture, the tetrachloroethane layer was separated and washed thoroughly with hot dilute hydrochloric acid and hot water. On standing overnight, the mixture yielded light fawn crystals (35 g.) (A), which were recrystallised from nitrobenzene to give colourless crystals of the dicarboxylic acid (LI), m.p. 299-301° (decomp.) (Found: C, 75.9; H, 4.2. $C_{30}H_{18}O_6$ requires C, 75.9; H, 3.8%). The crystals dissolved in concentrated sulphuric acid to give a red solution. The tetrachloroethane mother-liquor was extracted with hot ammonia solution. The extract, on acidification, yielded a brown solid (180 g.) (B) consisting of mixed isomeric acids.

Heptaphene-5:18-10:15-diquinone (LIV). - The acid (A) (20 g.) was dissolved in concentrated sulphuric acid (200 ml.) and heated to 155° for 2 minutes, the colour changing from red to an orange-red. When the solution was diluted with ice at 140°, yellow needles crystallised, which were filtered off and washed with hot ammonia solution and water. Sublimation at 370-380°/5 x 10^{-4} mm. followed by crystallisation from 1-methylnaphthalene gave bright yellow feathery needles (9.5 g.) of the diquinone (LIV) which decomposed without melting at 550° to give a black residue (Found: C, 82.2; H, 3.3. $C_{30}H_{14}O_4$ requires C, 82.2; H, 3.2%). The diquinone gave a reddish-orange solution in concentrated sulphuric acid; with alkaline sodium dithionite solution, it gave a violet red vat which became brown on boiling.

Heptaphene (LVII). - The diquinone (LIV) (6.4 g.) zinc dust (40 g.), and pyridine (200 ml.) were heated and acetic acid (80%; 150 ml.) was added dropwise over a period of 5½ hours. The colour of the solution changed from brown, through a reddish-orange, to a pale orange. A fine orange solid crystallised

out during the reaction. The suspension was decanted from the zinc dust and the solid (2 g.) filtered off and washed successively with pyridine, benzene and ether. Crystallisation from 1-methylnaphthalene gave light orange plates, m.p. 473-474° of heptaphene (LVII) (Found: C, 94.8, 95.0; H, 4.7, 5.0. $C_{30}H_{18}$ requires C, 95.2; H, 4.8%). In organic solvents it had a green fluorescence and dissolved to give a violet-red solution in concentrated sulphuric acid. When the pyridine mother-liquor from the above filtration was added to water, a precipitate formed which, after being washed and sublimed in vacuum, gave a further quantity of heptaphene (1.5 g.).

Maleic Anhydride Adduct (LVIII). - Heptaphene (0.1 g.) and excess of maleic anhydride were heated under reflux in xylene (20 ml.) until the solution became colourless. Concentration of the xylene gave colourless crystals of the dianhydride (LVIII) m.p. 292-296° (decomp.) (Found: C, 78.7; H, 3.8. $C_{38}H_{22}O_6$ requires C, 79.4; H, 3.9%).

Ring Closure and Reduction of the Isomeric Acids (B). - Treatment of the mixed acids (B) with sulphuric acid as above gave a dark greenish-yellow product which was reduced with zinc dust, pyridine and acetic acid.

When the pyridine solution was poured into water, a precipitate formed which was sublimed to give a reddish-orange mixture of hydrocarbons. No separation of the mixture could be achieved by crystallisation or by chromatography.

2:3-8:9-Dibenzopicene (LV). - The mixture of hydrocarbons was dissolved in 1-methylnaphthalene and small portions of maleic anhydride were added until the absorption bands of heptaphene and anthraceno-tetracene (LVI) were no longer seen when the solution was viewed spectroscopically. Crystallisation from the solution yielded pale yellow plates, m.p. 489-490°, of 2:3-8:9-dibenzopicene (LV) (Found: C, 94.5; H, 5.2. $C_{30}H_{18}$ requires C, 95.2; 4.8%). The crystals dissolved, on being heated, in concentrated sulphuric acid to give a yellowish-green colour which changed to olive-green. The solution in organic solvents had a strong blue fluorescence.

Synthesis of 2:3 Benzopicene and Naphtho(2':3'-1:2)chrysene.

Condensation of chrysene with o-Toluoyl chloride. - Powdered aluminium chloride (60 g.) was added during 4 min. to a mixture of chrysene (46 g.) and o-toluoyl

chloride (33 g.) in tetrachloroethane (60 ml.) at 95° and stirred for a further 5 min. The orange red mixture was cooled, decomposed, and diluted with more tetrachloroethane. The organic layer was washed successively with hot dilute hydrochloric acid, hot dilute aqueous ammonia, and hot water. The tetrachloroethane was distilled off and the residue pyrolysed at 400° for 15 min., to give a black solid (56 g.). 28 g. Of this were sublimed in a vacuum. Fractions were collected between 170° and 340° during 45 hr. The initial fractions (collected at 170-220°) were mainly unchanged chrysene. The later fractions (13 g.) were collected together and extracted with 150 ml. of warm benzene.

2:3-Benzopicene (LXI). - The residue (4.2 g.) from the above benzene extraction was crystallised from xylene, giving yellow plates (1.8 g.). Spectroscopy (bands at 472, 442 and 404 mμ) showed the plates to be a mixture of two compounds. Attempts to separate them by chromatography were unsuccessful. Several recrystallisations from 1:2:4-trichlorobenzene containing small quantities of maleic anhydride gave

pale yellow plates, m.p. 394-395°, of the benzopicene (LXI) (Found: C, 95.3; H, 5.1. $C_{26}H_{16}$ requires C, 95.1; H, 4.9%). The compound did not dissolve in concentrated sulphuric acid and had a blue fluorescence in xylene solution.

12:1'-Oxido-maphtho(2':3'-1:2)chrysene (LXVIII). - The above benzene extract was chromatographed on alumina with benzene as eluant. A first small colourless band gave a small quantity of chrysene. A second yellow band yielded yellow needles, m.p. 288-289° (Beyer and Richter (44) 285-286°) of the 12:1'-oxido-naphtho(2':3'-1:2)chrysene (LXVIII) (Found: C, 91.0; H, 4.2. $C_{26}H_{14}O$ requires C, 91.2; H, 4.1%). The compound was identical with that obtained as below by the reduction of naphtho(2':3'-1:2) chrysene-1':4'-quinone, and dissolved in concentrated sulphuric acid to a deep red solution.

2:3-Benzopicene-1:4-11:12-diquinone (LXII). - Chromium trioxide (0.26 g.) in water (1 ml.) was added to a suspension of benzopicene (0.1 g.) in acetic acid (6 ml.). After 3 hr. under reflux the suspension was filtered and the orange powder crystallised from nitrobenzene as orange feathery needles of the diquinone (LXII), m.p. 387-388° (Found:

C, 80.6; H, 3.5. $C_{26}H_{12}O_4$ requires C, 80.4; H, 3.1%). The compound gave an orange vat with alkaline sodium dithionite and dissolved in concentrated sulphuric acid to a reddish-brown solution.

An excess of hydrazine hydrate was added to a suspension of the diquinone (LXII) in hot pyridine. The reddish-orange suspension changed to deep red and the diquinone dissolved completely. The solution was heated under reflux for 20 min. and the pyridine was concentrated to small bulk but no crystallisation took place. The light-brown precipitate, formed on addition of water and boiling, crystallised from nitrobenzene as orange needles identical with the benzopicenediquinone (LXII).

An excess of o-phenylenediamine (10 mg.) and the diquinone (LXII) (14 mg.) in nitrobenzene (3 ml.) were heated under reflux for 30 min. The dark yellow crystals (13 mg.) obtained were recrystallised from nitrobenzene, to give fine yellow needles, m.p. 363-364°, of the phenazine (LXV) (Found: N, 5.9. $C_{32}H_{16}O_2N_2$ requires N, 6.1%). The compound gave an orange-red vat in alkaline sodium dithionite and dissolved in concentrated sulphuric acid to a violet-red solution.

2-o-Carboxybenzoylchrysene (LXIX). - Powdered aluminium chloride (117 g.) was added, during 5 min., to phthalic anhydride (64 g.) and chrysene (80 g.) in tetrachloroethane (200 ml.) at 90°. The mixture became reddish-orange and the temperature rose to 98°. The reaction quickly subsided and, after decomposition, the tetrachloroethane layer was separated and washed with dilute hydrochloric acid and hot water. The tetrachloroethane solution was extracted with rather concentrated ammonia solution which precipitated an ammonium salt. Acidification of this salt gave an acid (80 g.) which on being recrystallised several times from acetic acid gave colourless needles, m.p. 206-211° (Beyer and Richter (44), m.p. 213-214°), of 2-o-carboxybenzoylchrysene. The mother-liquor from the ammonium salt, on acidification, yielded another portion of acid product (24 g.) (Found: C, 82.8; H, 4.6. Calc. for $C_{26}H_{16}O_3$ C, 83.0; H, 4.3%).

Naphtho(2':3'-1:2)chrysene-1':4'-quinone (LXX). - A solution of 2-o-carboxybenzoylchrysene (60 g.) in benzoyl chloride (180 ml.) was heated under reflux. Concentrated sulphuric acid was added dropwise at

intervals until a transient blue colour no longer appeared. The solution was boiled for a further 10 min. Orange needles (23 g.) crystallised from the solution on cooling. Recrystallisation from xylene gave orange needles, m.p. 273-274°, of the quinone.

Naphtho(2':3'-1:2)chrysene (LXVII). - The quinone (LXX) (5 g.), zinc dust (5 g.) and pyridine (70 ml.) were heated under reflux and 80% acetic acid (80 ml.) was added during 5 hr. The solution was filtered into water, and the precipitate was heated above its m.p. in a vacuum, powdered, and chromatographed in benzene on alumina with benzene as eluant. A first colourless band yielded colourless plates, m.p. 187-188° (Beyer and Richter (44), 185-186°), of naphtho(2':3'-1:2)chrysene. A second yellow band yielded yellow needles, m.p. 288-289°, of the compound (LXVIII).

When the acid (24 g.) from the mother-liquor of the crystallised ammonium salt of the 2-o-carboxybenzoyl-chrysene was cyclised and the mixture of the quinones reduced as above, a mixture of benzopicene (LXI) and naphthotetracene (LXIV) (identified by its spectrum) was obtained. This indicates that under the latter condition described some phthalic anhydride reacts with a side ring of chrysene.

APPENDIX.

Crystal Data for Circumanthracene (XV).

Measurement of the grey black prismatic needles with copper Kα radiation (λ 1.54Å) showed that they are monoclinic with $\underline{a}$ = 23.77 ± 0.01, $\underline{b}$ = 4.59 ± 0.03, $\underline{c}$ = 9.98 ± 0.01Å, $\beta = 99^{\circ}54' \pm 30'$.

The ($\underline{h}0\underline{l}$) spectra are absent when $\underline{h}$ is odd, and (0$\underline{k}$0) when $\underline{k}$ is odd. The space group is uniquely determined as $P2_1/a$ (C^5_{2h}). The volume of the unit cell is 1075 ± 6Å^3. The density of the crystals measured by flotation in potassium iodide solution at 20° is 1.52 ± 0.01.

The space group $P2_1/a$ requires four asymmetric molecules or two centrosymmetric molecules per unit cell. If we assume two molecules, then the molecular weight can be found from the above data in the following way.

Volume of unit cell = 1075Å^3 = 1075 x 10^{-24} c.c.

$\therefore$ 1 c.c. contains $\frac{10^{24}}{1075}$ unit cells.

$\therefore$ $\frac{2 \times 10^{24}}{1075}$ molecules weigh 1.52 g.

$\therefore$ 6.0228×10^{23} (Avogadro Na) molecules weigh

$$1.52 \times \frac{1075}{2 \times 10^{24}} \times 6.0228 \times 10^{23}$$

$\therefore$ Molecular Weight = 492

More detailed evidence regarding the structure is obtained by comparing the crystal data with those for coronene and ovalene.

Crystal Data

	a(Å)	b(Å)	c(Å)	β	Space group	Z	d	M.
Coronene $C_{24}H_{12}$	16.1	4.70	10.2	110.8°	$P2_1/a$	2	1.38	300
Ovalene $C_{32}H_{14}$	19.5	4.70	10.1	105.0°	$P2_1/a$	2	1.49	398
Circumanthracene $C_{40}H_{16}$	23.8	4.59	10.0	99.9°	$P2_1/a$	2	1.52	496

The b and c axes for the crystals remain very constant but there is a steady increase in a and decrease in β as we pass from coronene to circumanthracene. This is strong evidence that all these crystals are of the same structural type, a conclusion which is confirmed in detail by a study of the X-ray spectra.

By setting up a trial structure based on the analogy with coronene and ovalene it was found that most of the (h0l) structure factors could be explained. A Fourier synthesis based on this trial structure yielded a very clear electron - density projection of the molecule, which showed all the carbon atoms in the positions expected from structure (XV). At the present stage of refinement the discrepancy between calculated and observed structure factors has been reduced to about 19%. At this point there can now be no reasonable doubt that the structural formula is correct.

BIBLIOGRAPHY

(1) Clar, Ber., 1936,69,607.

(2) Clar, Ber., 1949,82,495.

(3) Clar, Arom.Kohl., 2. 1952, p. 25.

(4) Clar, J.Chem.Phys., 1949,17,741.

(5) Clar, Spectrochim.Acta, 1950,4,116.

(6) Clar and Guzzi, Ber., 1932,65,1521.

(7) Wright, Ph.D. (Glasgow) 1949, p. 19.

(8) Clar, Arom.Kohl., 2. 1952, p. 359.

(9) I.G. Farbenind.A-G., G.P., 652,912 (1927).
G.P., 555,180 (1929).

(10) Dewar, J.Chem.Soc., 1952,3539.

(11) Guyot and Staehling, Bull.Soc.chim., 1905,33,1104.

(12) Zinke, Funke and Pongratz, Ber., 1925,58,799.

(13) Scholl and Meyer, Ber., 1934,67,1229.

(14) Clar and Furnari, Ber., 1932,65,1421.

(15) Clar, Ber., 1932,65,846.

(16) Clar and Zander, J.Chem.Soc., 1957, 4615.

(17) Brockmann and Randebrock, Chem.Ber., 1951,84,533.

(18) Brockmann, Proc.Chem.Soc., 1957,306.

(19) Scholl and Meyer, Ber., 1934,67,1229

(20) Scholl, Meyer and Winkler, Ann., 1932,494,220.

(21) Baddeley, J.Chem.Soc., 1949,S1,99.

(22) Fromherz, Thaler and Wolf, Z.Elektrochem., 1943,49,387.

(23) Clar and Stewart, Ph.D., (Glasgow), 1953, p. 77.

(24) Clar, Chem.Ber., 1949,82,59.

(25) Clar and Wright, Ph.D. (Glasgow), 1949.
Arom.Kohl., 2. 1952, p. 290.

(26) Willemart, Compt.rend., 1935,201,1201.

(27) Clar, Ber., 1940,73,351.

(28) Clar, Ber., 1948,81,52.

(29) Clar and Engler, Ber., 1931,64,1597.

(30) Fieser, Experiments in Org.Chem. 2nd Ed. p. 459.

(31) Linstead and Thomas, J.Chem.Soc., 1940,1127.

(32) Zinke, Nusmüller and Ott, Monats.Chem., 1955,86,853.

(33) Zinke,Pack,Ott and Weisenberger, Monats.Chem., 1951,
82,384.

(34) Clar, Arom.Kohl., 2. p. 70.

(35) Mosettig and van de Kamp, J.Amer.Chem.Soc., 1930,52,3704

(36) Bachmann, J.Amer.Chem.Soc., 1935,57,535.

(37) Clar and Kelly, Unpublished work.

(38) Clar, Chem.Ber., 1948,81,68.

(39) Clar, Arom.Kohl., 2. p.142

(40) Clar and Stewart, J.Chem.Soc., 1951,3215.

(41) Clar and Lombardi, Ber., 1932,65,1417.

(42) Clar, Ber., 1940,73,599.

(43) Beyer, Ber., 1938,71,913.

(44) Beyer and Richter, Ber., 1940,73,1319.

(45) Cook and Graham, J.Chem.Soc., 1944,329.

(46) Carruthers, J.Chem.Soc., 1953,3486.

(46a) Clar, Ber., 1929,62,1574.

(47) I.G. Farbenind, A.-G., G.P., 652, 912.
Ges. Chem. Ind in Basel, Swiss P 179, 440
Chem. Zentr. 1936, I, 2637
1938, I, 2064.

(48) Scholl, Bottger and Wanka, Ber., 1934, 67, 603.

(49) Gilman, Zoellner and Selby, J. Amer. Chem. Soc., 1933, 55, 1252.

(50) Woodward et al., J. Amer. Chem. Soc., 1941, 63, 3229.

Arom. Kohl. 2 = Aromatische Kohlenwasserstoffe,
Springer-Verlag (Berlin),
Edition 2 (1952).